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EFFECT OF DIVALENT IONS IN
ENHANCED OIL RECOVERY

by

Nader Agharazi-Dormani

A thesis presented to the School of Graduate Studies
in partial fulfillment of the requirement for the
degree of

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UNIVERSITY OF OTTAWA

ABSTRACT

During the last ten years, Canada has consumed more petroleum than she has produced. To reduce this dependency on politically unstable supply of foreign oil, alternative domestic sources must be developed. Heavy oil and tar sands are expected to only partially offset Canada's dependency on imported oil. This is where Enhanced Oil Recovery (EOR) prospects seem the brightest.

Petroleum occurs in underground reservoirs with some so-called connate water which contains monovalent ions such as Na^+ and Cl^- and in most cases also divalent ions like Ca^{++} and Mg^{++}. These divalent ions have been known to increase the interfacial tension (IFT) between the water phase and the oil phase in tertiary oil recovery when surfactants are used to displace the oil. Furthermore, divalent ions are considered to cause complications in reservoir flooding. This is because they form precipitates with surfactants and insoluble hydroxides with the alkali used in caustic flooding.

In this study, interfacial tensions between a Canadian light crude oil (from Chatham, Ontario) and various connate waters, containing different ion concentrations, were measured both with and without surfactants present. Oil recovery tests were then conducted in model porous media composed of very fine glass particles. To prepare the porous medium, the core holder was filled with connate water and packed with the glass beads using a wet packing technique. The cell was then flooded with oil until the initial oil saturation (irreducible water saturation) was reached.

Oil recovery experiments were carried out using two strategies. Strategy I consisted of first flooding the porous medium with 4-5 pore volumes (PV) of the same connate water until no more oil could be recovered, followed by 3-4 pore volumes of surfactant solution. In strategy II, the oil-saturated cell was flooded directly with 5-6 pore volumes of surfactant until no more oil was produced. It was found that when divalent ions were present in the connate water, the tertiary recovery was higher, despite the greater oil-water IFT.

The capillary numbers (N_{ca}) and ionic strengths (IS) for the different systems were calculated. The relationships between the oil recovery, IFT, N_{ca} and IS, were then examined in detail .

To explain the unexpectedly high tertiary recoveries observed in systems with divalent cations, two distinct mechanisms, namely "pore blockage" and "ganglia formation", were proposed and discussed .

ACKNOWLEDGMENT

I wish to thank my two research supervisors, Drs. V. Hornof and G. Neale, for their invaluable guidance and assistance during the course of the experimental work as well as during the preparation of this thesis.

I would also like to thank Mr. G. Gasperetti, and his able technical team Messrs. D. Lefebvre and A. Bonaldo, for their wonderful assistance in the fabrication and installation of the experimental equipment.

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PART I

INTRODUCTION AND LITERATURE SURVEY

CHAPTER I

INTRODUCTION

Petroleum is the main energy source in Canada and in almost all other countries. Over 70,000 by-products, of a very wide range, are produced from petroleum. The many inter-relationships between petroleum and our everyday life have made us dependent on oil to a very great extent.

Unfortunately, at present rates of consumption, the proven oil reserves of the world recoverable by today's technologies will only provide a 30-40 year supply. The situation in Canada is even less hopeful because Canadian reserves will be depleted by 1998 (Table 1). The geopolitical instability of the oil-rich middle eastern countries makes the future economics and market of oil so uncertain that we must look for alternative sources and recovery technologies . In Canada, tar sands and heavy oils are two such resources. However, economic as well as technological restraints have made the utilization of these sources quite limited. Enhanced oil recovery (EOR) clearly offers one of the best chances for reducing Canada's dependency on foreign oil.

Table 1 : Crude Oil Reserves and Demand (1)

Proven Reserves	Million Barrels
Canada :	
Light	7020
Heavy	2305
World	668,262
Annual Demand	
Canada	519
World	21,325

Crude oil reservoirs contain a mixture of water, oil and gas in the pores of the reservoir rock, bounded both below and above by an impervious rock formation such as granite or shale (Fig 1) .

The interstitial (connate) water usually contains a mixture of monovalent and divalent ions. The oil is trapped in the pores by natural forces resulting from viscosity, capillary and interfacial tension effects. For oil to be recovered these forces have to be overcome .

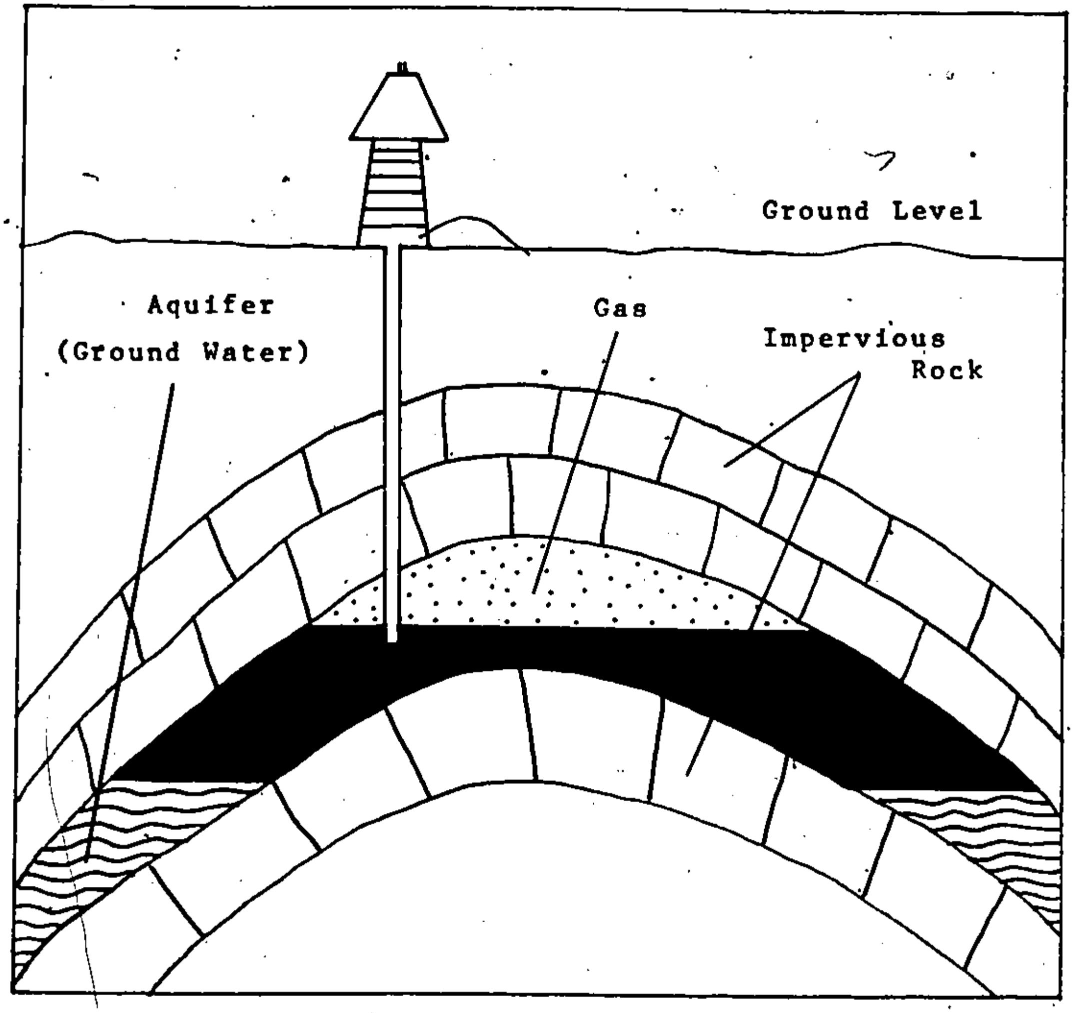


Fig. 1- A Typical Oil Reservoir

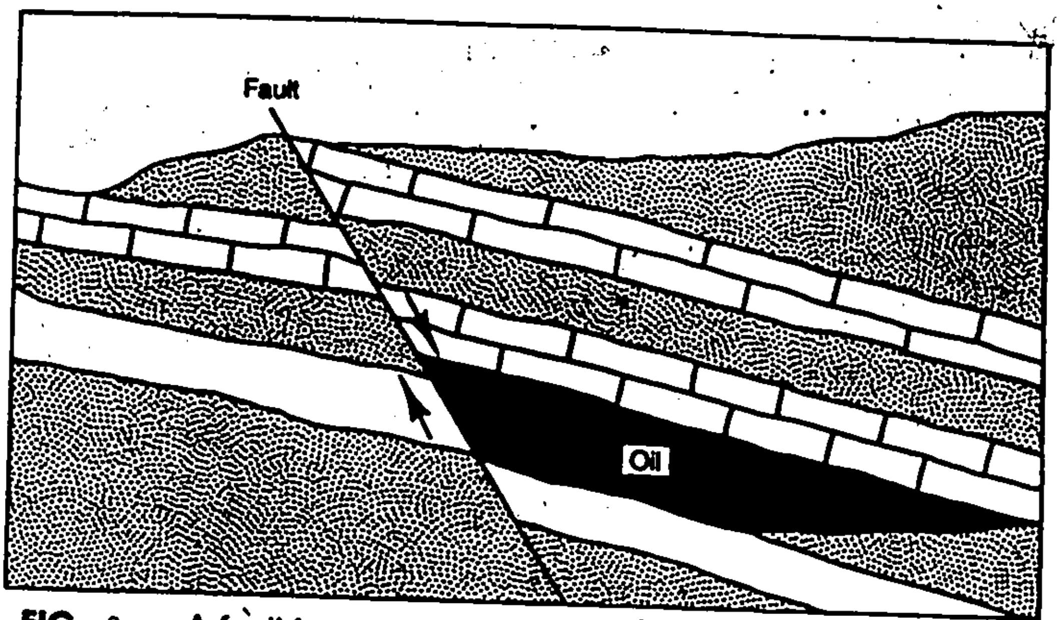


FIG. 2- A fault is a crack in the earth along which layers move.

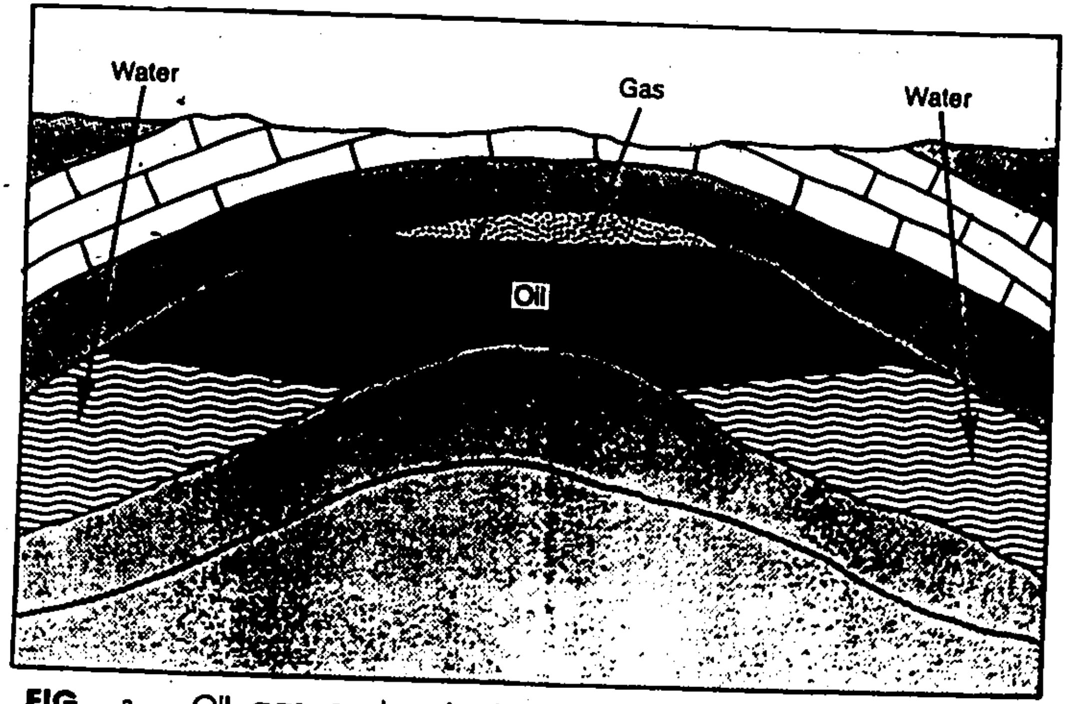


FIG. 3- Oil, gas, and water tend to separate into three layers. (49)

1.1- Primary Recovery

Conventional methods of oil production relying on internal reservoir pressure are designated Primary Recovery. In the early stages of oil recovery from a new oil field, much of the pressure required to force the oil to the surface is obtained from the confined fluids (caused by hydrostatic pressure of the surrounding aquifer, and / or the pressure of gases dissolved in the oil) . However, continued production results in decreased reservoir pressure to a point where it becomes necessary to use pumps to "lift" the oil from the well to the surface. The primary recovery stage typically produces 10-30% of the original oil-in-place (OOIP) from conventional oil reservoirs.(2)

1.2- Secondary Recovery

The decreasing force available to drive the oil into the well-bore, as well as the pressure of the gas in the emptied pore space, adversely affect the oil production. To overcome the drop in internal pressure, external energy must be supplied to the reservoir. A technique called "pressure maintenance" will accomplish this task. It consists of injection of large volumes of water (or in some cases gas) through another well, the so-called <u>injection well</u>. The injected fluid will force the oil out of the porous rock towards the production well. It will restore the pressure in the reservoir and help to keep the dissolved gases in solution at the same time (something which will result in maintaining a low oil viscosity). To improve the performance of water flooding, a number of reagents such as acids, alkalis, salts and polymers can be added (Fig. 4 5). These processes are collectively termed secondary recovery processes.

Fig.(6) shows a plane view of some of the patterns in which injection wells are customarily drilled around the production wells. Secondary production techniques may produce anywhere from 15 to 30 % additional recovery of the OOIP. In other words, 40-75 percent of OOIP still remains in the reservoir after completion of primary and secondary recovery processes.

1.3- Tertiary Recovery

Water flooding works quite well in displacing oil from reservoirs and it is also relatively inexpensive. However, since the early 1970's, the number of prospective North American fields in which water flooding could be applied has been declining. The next step to maintaining oil production is to recover a "third crop" of oil from those fields which have already under-gone primary and secondary recoveries . To accomplish this, there are a number of various techniques which are collectively called Tertiary Recovery or Enhanced Oil Recovery (EOR) methods.

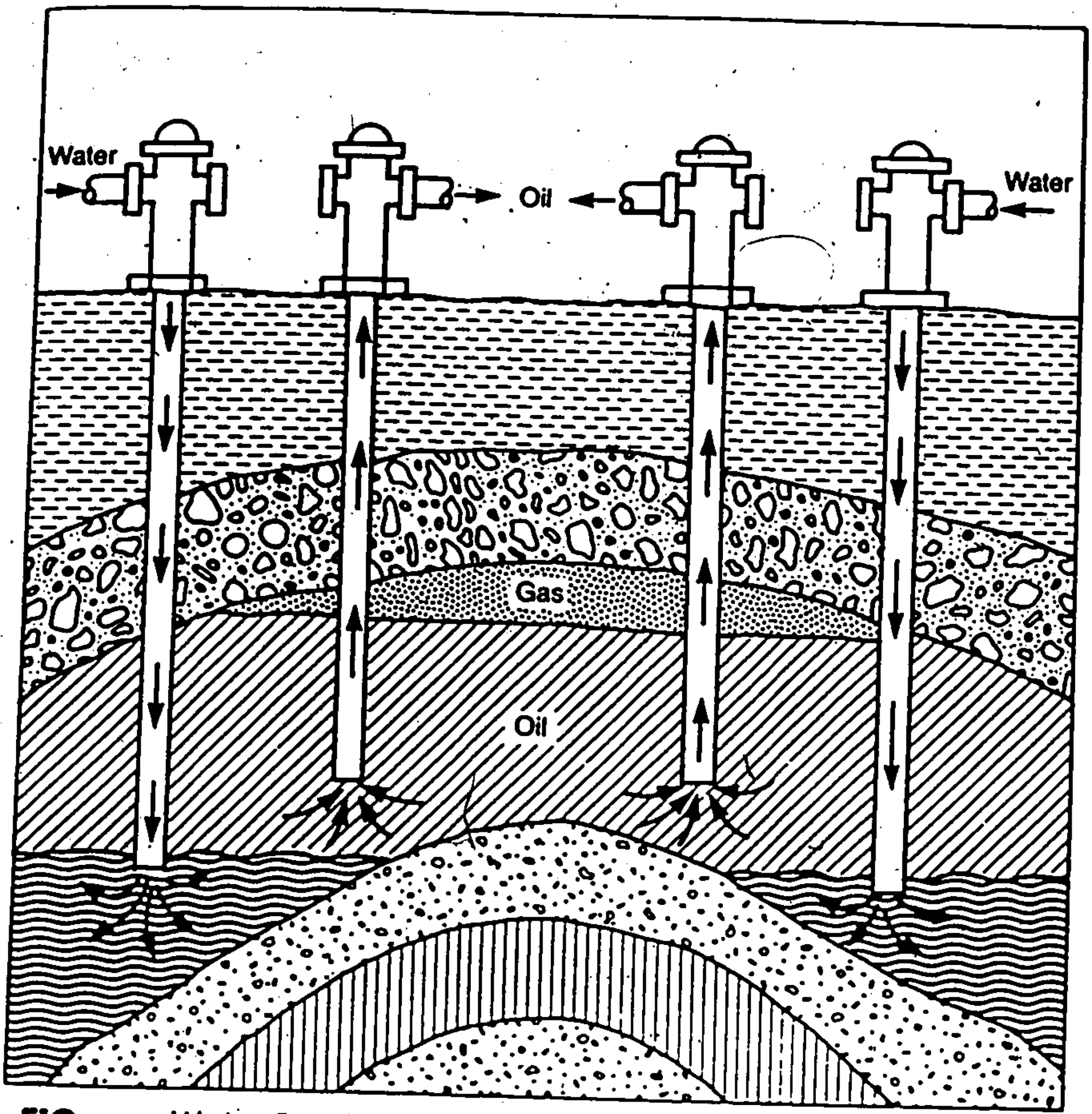


FIG. (4a)-Water-flood technique. (49)

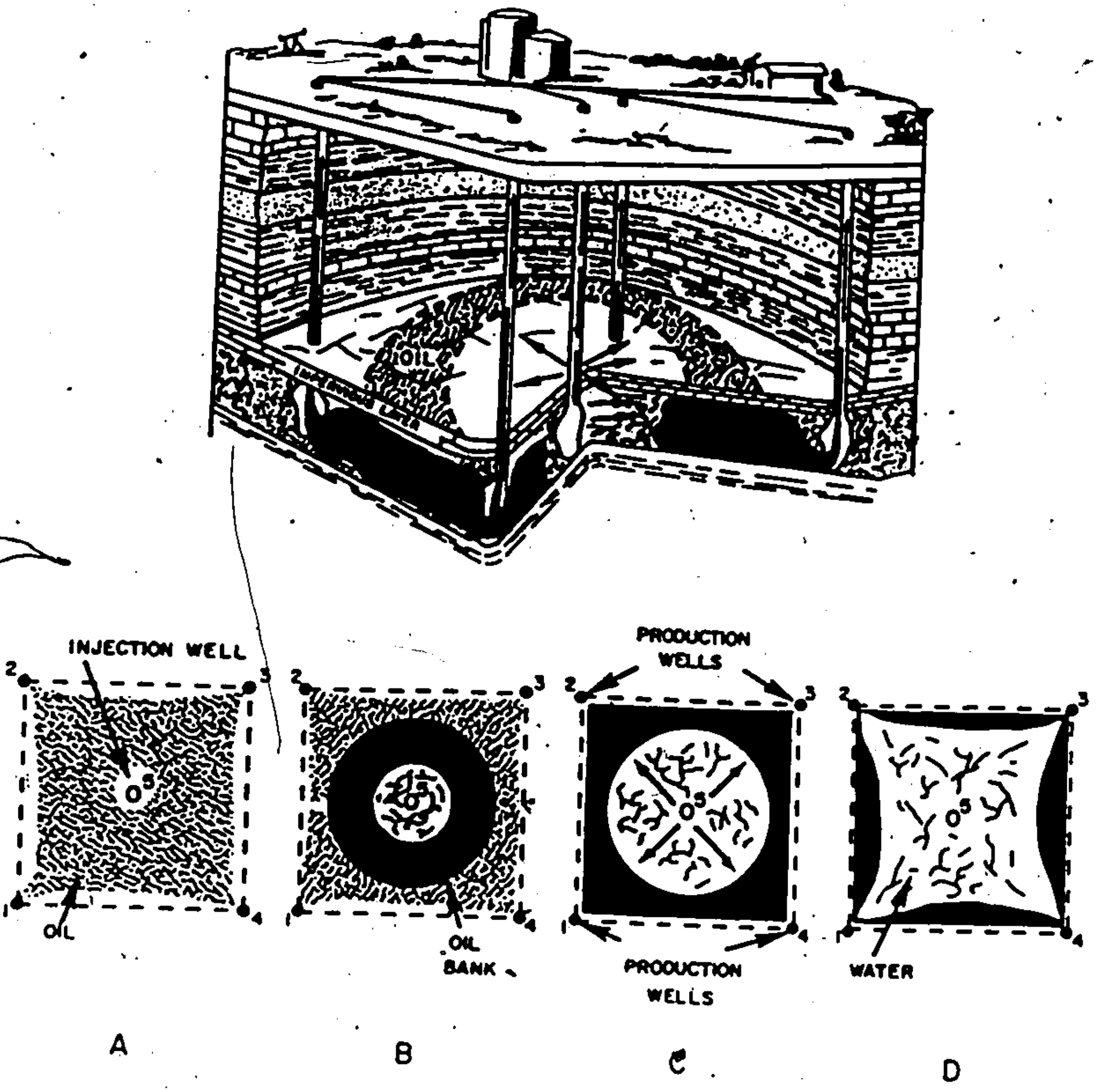
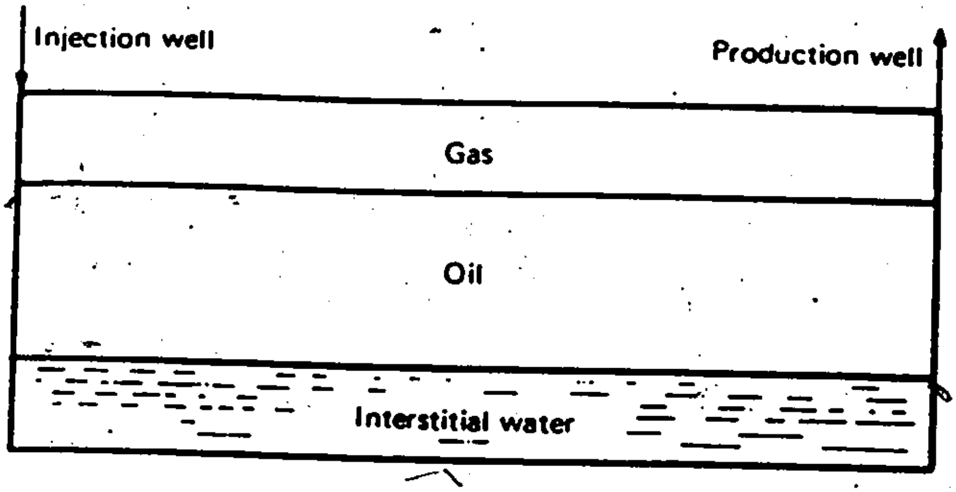
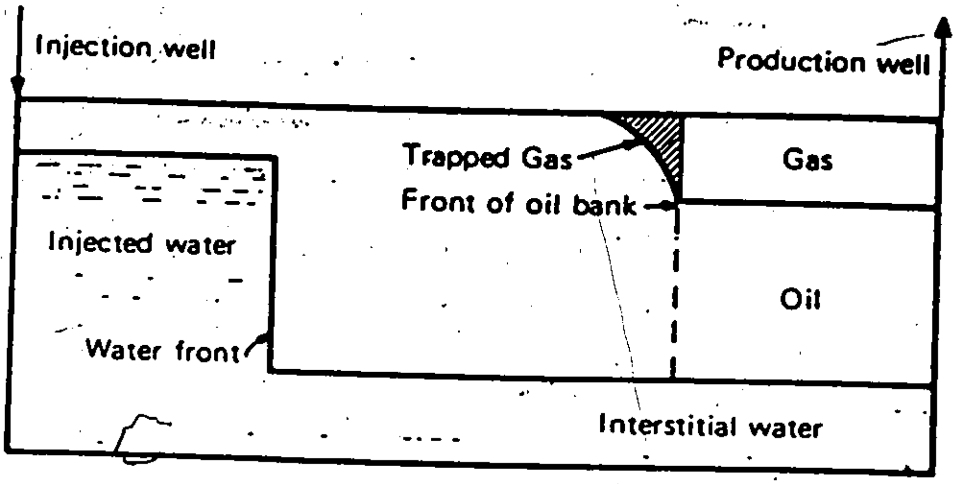


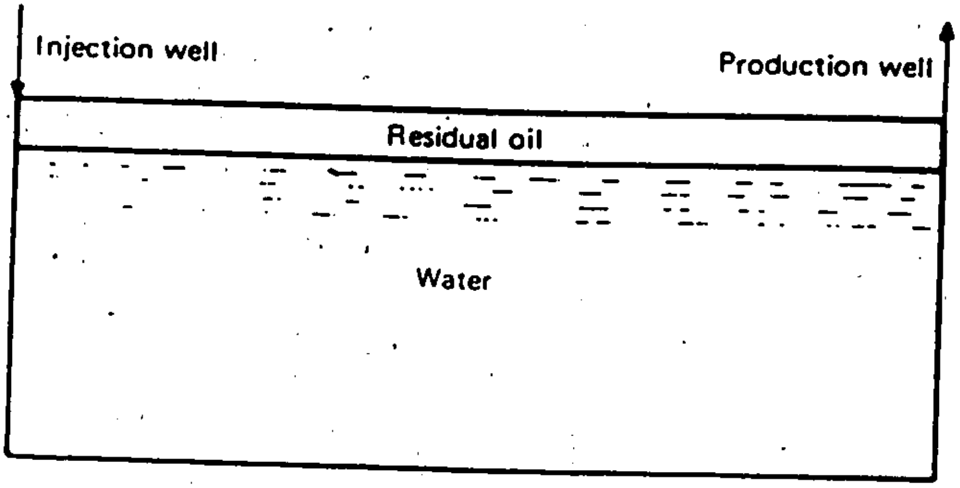
Fig. (4b)-Schematic diagram of an oil reservoir and the displacement of oil by water or chemical flooding. (9)



BEFORE WATER INJECTION

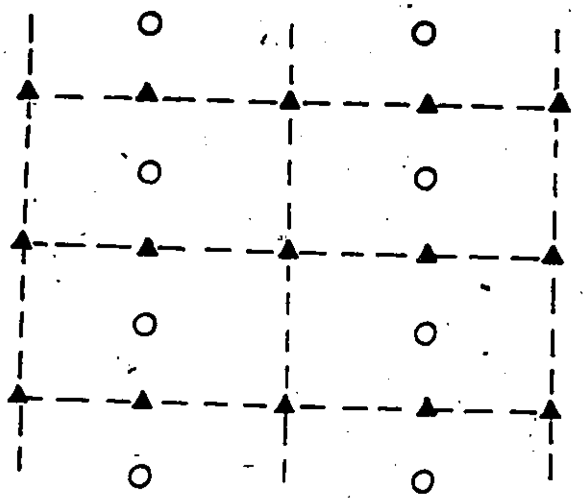


DURING WATER INJECTION

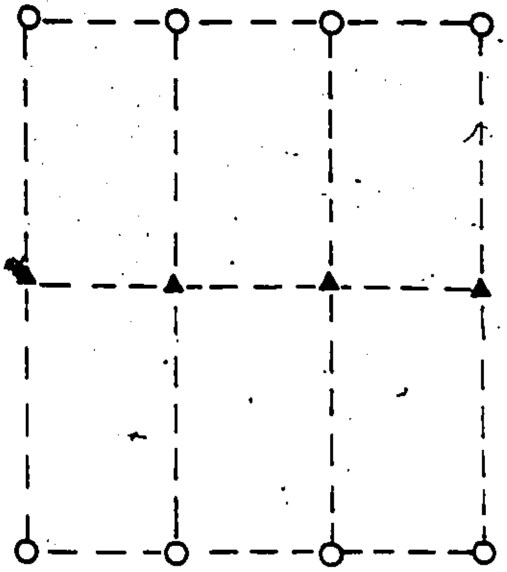


AFTER WATER INJECTION

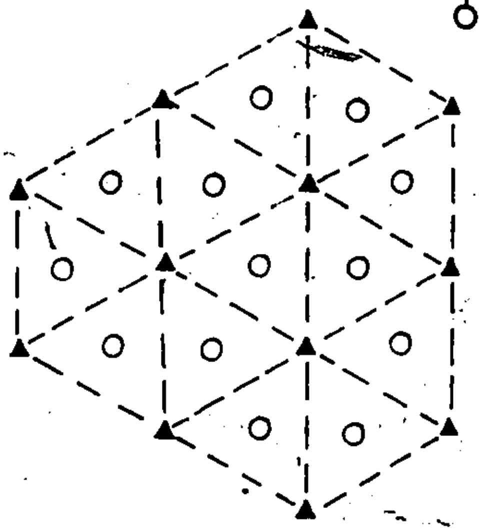
Fig. 5 - Waterflooding (48)



Normal Nine-Spot



Direct Line Drive

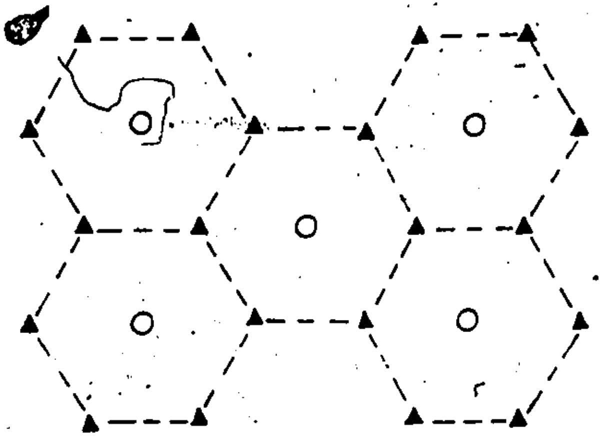


▲ Injection Well

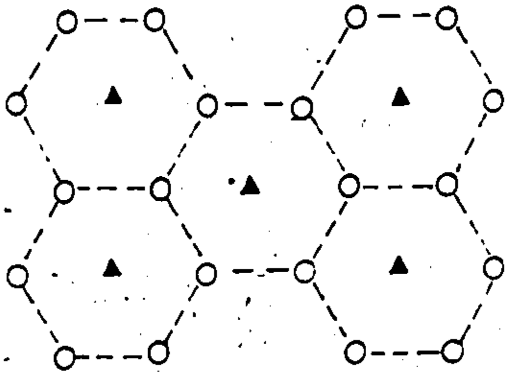
○ Production Well

— — — Pattern Boundary

Skewed Four-Spot



Seven-Spot



Inversed Seven-Spot

Fig. 6- Flooding Patterns

1.4- Enhanced Oil Recovery (EOR)

Jha (2) has defined EOR as "all the techniques used to increase the amount of oil obtained after primary recovery ". A broader definition which has been adopted by the Alberta Energy Resources Conservation Board, states that "EOR is any oil production via artificial supplementation of natural reservoir energy"(3). By these definitions, EOR methods include :

- Pressure maintenance and waterflooding
- Steam flooding
- CO_2 injection
- Miscible fluid displacement
- Alkaline injection
- In situ combustion
- Steam stimulation
- Polymer injection

Fig (7) is a classification of these and other related recovery methods. However, since this research project is concerned only with surfactants and the effect of ionic species, we will not discuss those methods which are irrelevant to our study.

In many cases, procedures that may increase the sweep efficiency, can actually reduce the displacement efficiency. One the major challenges in any EOR project is to find an optimal mix of all the contributing factors. They could include and depend upon physical and geological properties of the reservoir and the fluids used, as well as temperature pressure conditions and above all, past production history and methods. From technical and economic points of view, the feasibility of an EOR process depends upon three important factors :

a) The residual oil saturation after primary recovery (S_{or}).
b) The displacement efficiency of the displacing fluid.
c) The volumetric sweep efficiency.

a) The Residual Oil Saturation

The amount of oil left in the reservoir after primary recovery is referred to as the residual oil and its ratio with the OOIP is called the residual oil saturation (S_{or}). Depending upon the wetting properties of the porous medium, this oil is in two forms. If the reservoir is an oil-wet one (Fig.8-a), the residual oil is generally in the form of thin

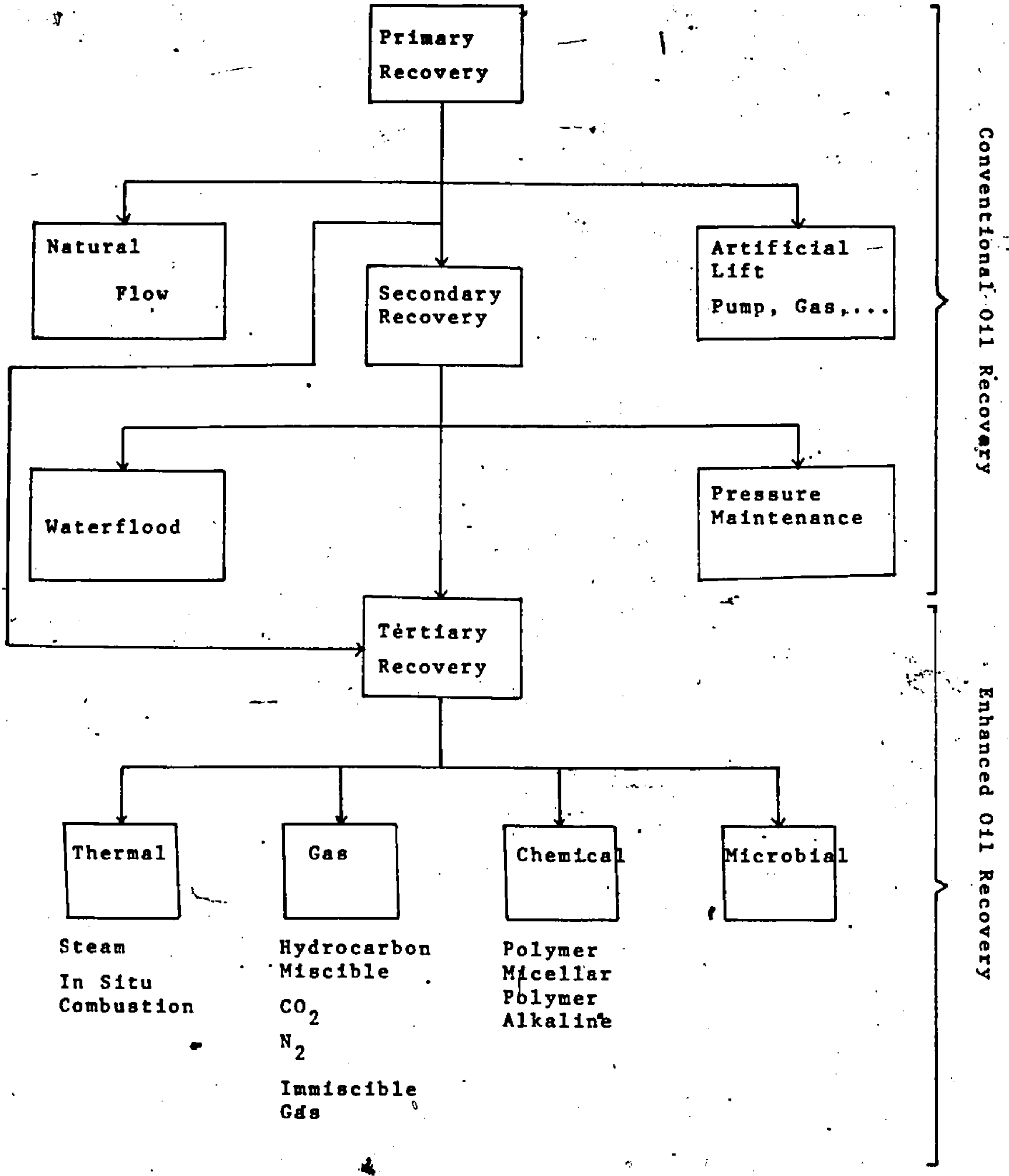


Fig. 7 - Recovery Mechanisms

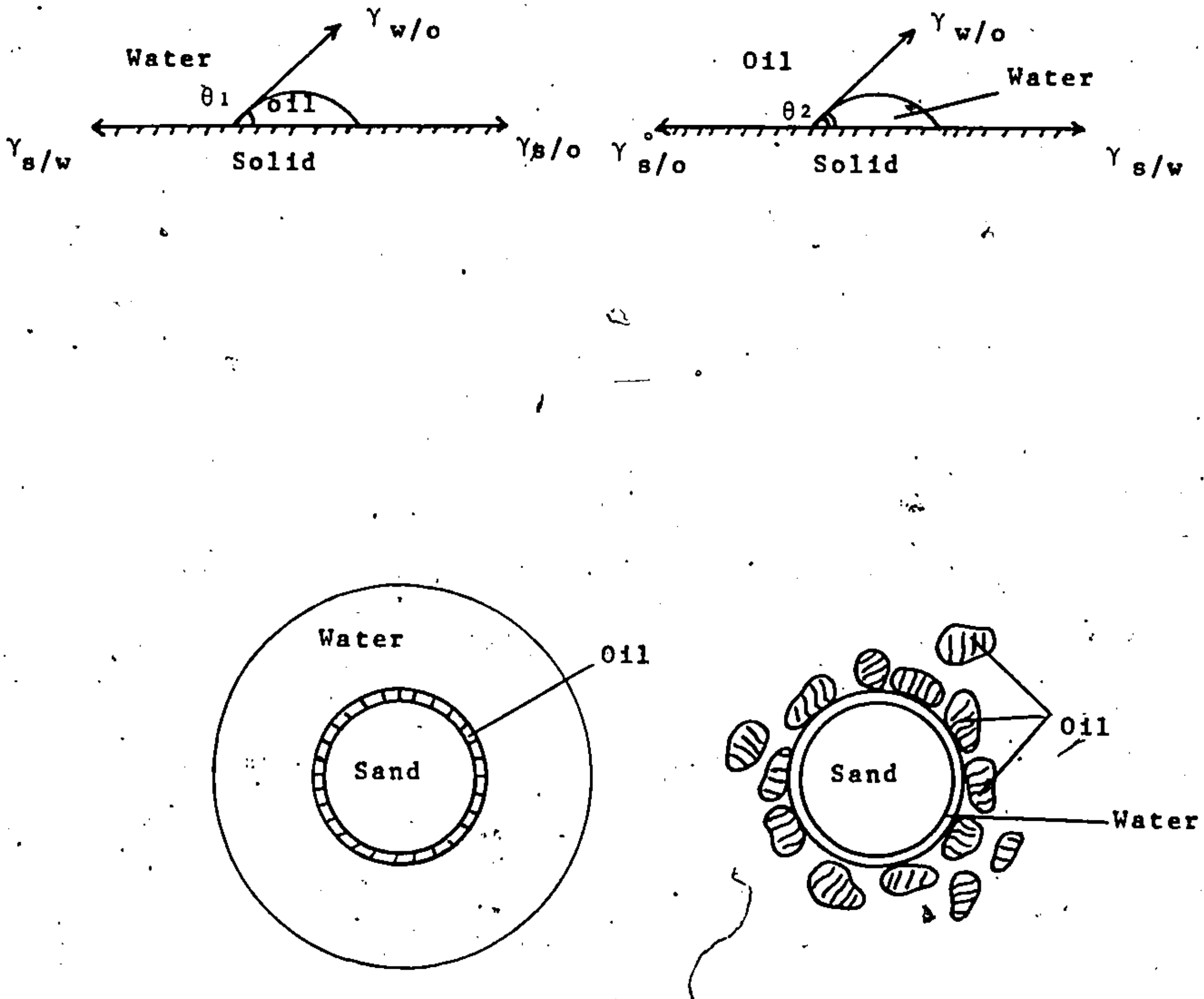
layer spread over the reservoir rock. conversely, in a water-wet reservoir, it appears as droplets of oil surrounded by connate water (Fig. 8-b ,9-a).
This fundamental difference between oil-wet and water-wet reservoirs leads to two different recovery patterns during a water injection process (Fig. 9-b).

It is appropriate at this stage to define the wettability itself. The wettability is the "relative affinity of the coexisting oil and water phases to adhere to the surface of the rock. If the rock is predominantly in contact with water, it is said to be preferentially water-wet. If oil covers the rock predominantly, it is referred to as oil-wet" (2). The ability of a liquid to wet a solid surface is measured by the so-called <u>spreading coefficient</u>.

$$S = \gamma_s - (\gamma_l + \gamma_{sl}) \qquad (1)$$

Where

γ_s : Surface energy per unit area of the solid (against air)
γ_l : Surface energy per unit area of the liquid (against air)
γ_{sl} : Surface energy per unit area of the solid-liquid interface



(a) Oil-wet $\theta_1 < \theta_2$

(b) Water-wet $\theta_1 > \theta_2$

Fig. (8a) - Oil-wet and Water-wet Sands

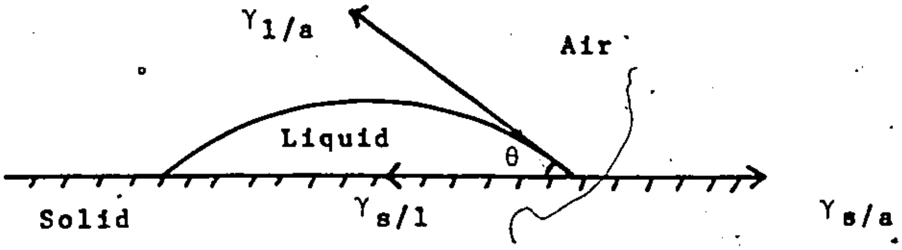


Fig. (8b) - Equilibrium Between Forces Acting on a Drop of Liquid on a Solid Surface

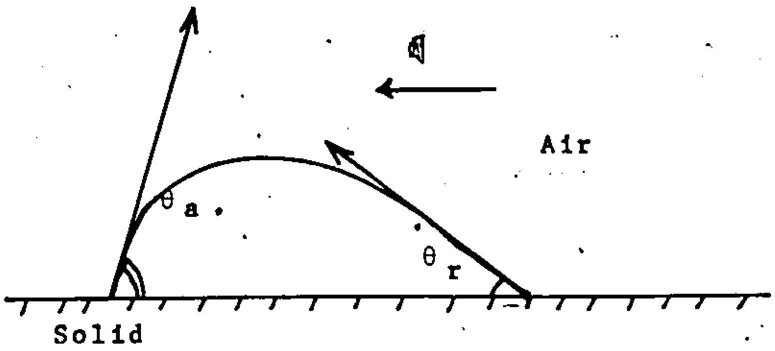


Fig. (8c) - Advancing and Receding Contact Angles

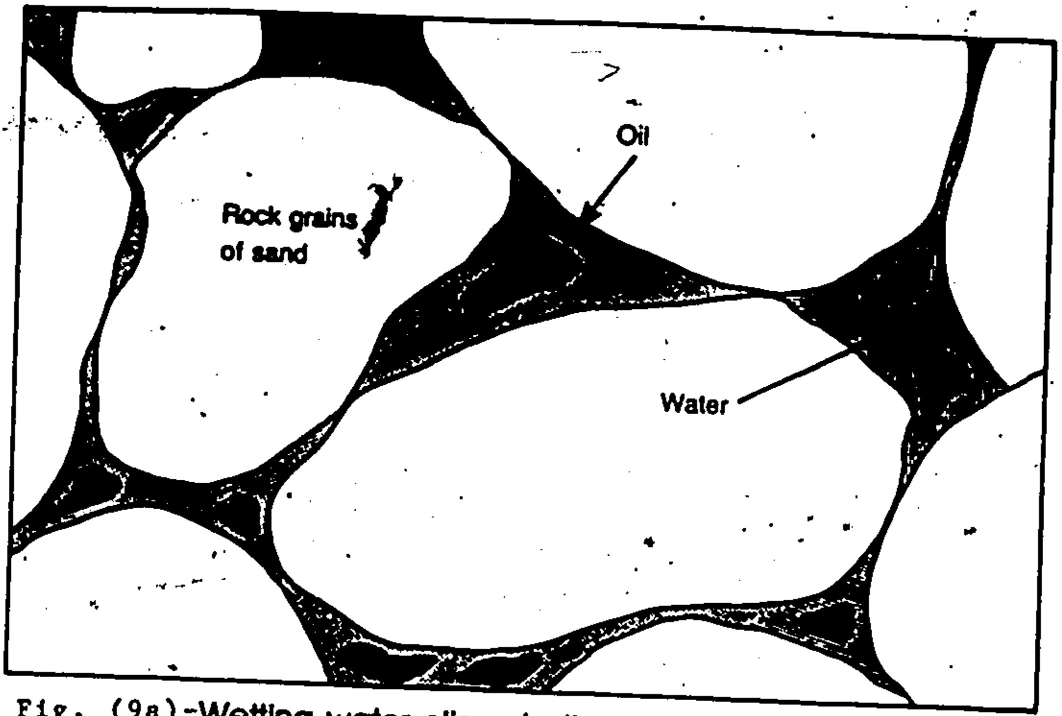


Fig. (9a)-Wetting water clings to the rocks, making them water wet. (49)

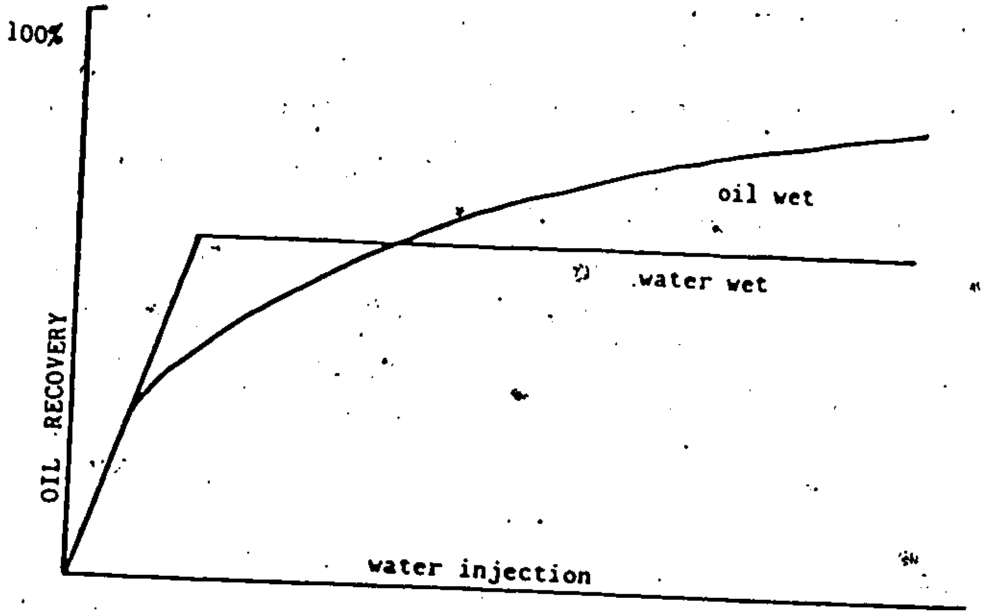


Fig. (9b)- Production History Curve (49)

If S is positive, a liquid should spread spontaneously over the solid. On the other hand, at equilibrium we know that :

$$\gamma_{w/o} \cos\theta = \gamma_{s/o} - \gamma_{s/w} \qquad (2)$$

If $\theta < 90$, the surface is water-wet . Lowering the oil water interfacial tension, will make a water-wet surface more water wet.'

b) The microscopic displacement efficiency

This quantity is the fraction of the initial oil saturation (S_{oi}) that is displaced from the reservoir pores, namely :

$$E_m = \frac{1 - S_{or} - S_{wi}}{1 - S_{wi}} \qquad (3)$$

Where :

S_{wi} Irreducible water saturation (the fraction of pore volume containing water at infinite capillary pressure).

The Capillary Pressure is defined as

$$P_c = \gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \qquad (4)$$

Where :

γ = Interfacial tension

and r_1, r_2 = Principal radii of curvature of the oil-water meniscus.

c) Volumetric sweep efficiency

This quantity is defined as the product of the aerial and vertical sweep efficiencies and is a function of the physical properties of the porous medium (such as permeability, porosity and mobility ratio of the injected fluid to the displaced fluid). Mobility is a measure of the ease with which a fluid flows through a porous medium, and is defined by :

$$\lambda = \frac{K}{\mu} \qquad (5)$$

Where the permeability of the porous medium , K, is defined by the well-known Darcy Equation ; .

$$u = -\frac{K}{\mu}\,dp/dx \qquad (6)$$

Where:

u = Average velocity of the fluid

p = Pressure drop along the porous medium

x = Length of the porous medium

K = Permeability of the formation

Mobility ratio is defined as :

$$M = \frac{\text{Mobility of the displacing phase}}{\text{Mobility of the displaced phase}}$$

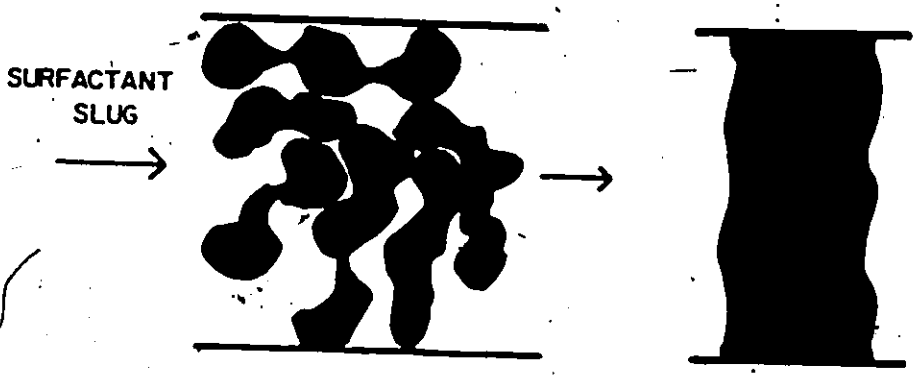
Viscous and Capillary Forces in EOR

As already mentioned, viscous forces expressed in terms of the mobility of the displacing and displaced phases are very important factors in EOR . To fully understand the role of the viscous forces in oil recovery, one should first have an understanding of sweep and displacement efficiencies as well as the concept of contact factor. Bansal (5) has discussed these properties in detail. On the other hand, as Wagner and Leach (6) and Mungan (7) have reported, the interfacial tension between the oil and water phases has to be reduced to about 10^{-2} to 10^{-3} mN/m in order to obtain increased oil recovery. The IFT in a natural reservoir is much higher than these values. As we will see later, surfactants increase the oil recovery primarily by lowering the IFT values.

Figure (10) shows the role of ultra-low IFT in promoting the mobilization of oil ganglia in porous media. These displaced oil ganglia must coalesce to form an oil bank (Fig. 11) and then it has to propagate without increasing the entrapment of the oil at the trailing edge of the oil bank as shown in Fig. 12. If this oil bank is formed early in the recovery process, the subsequent "snowball effect" will result in a good recovery. On the other hand, late formation of the oil bank will cause a poor recovery (Fig. 13).

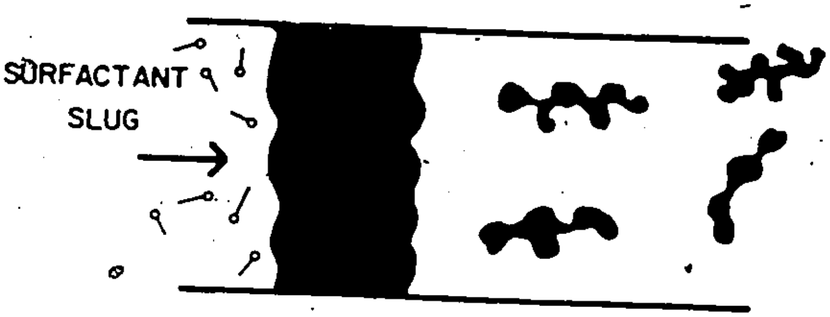
FOR THE MOVEMENT OF OIL THROUGH NARROW NECK OF PORES, A VERY LOW OIL/WATER INTERFACIAL TENSION IS DESIRABLE ≃ .001 DYNES/CM

Fig. 10 - Schematic diagram of the role of low interfacial tension in the surfactant (9) flooding process.



DISPLACED OIL GANGLIA MUST COALESCE TO FORM A CONTINUOUS OIL BANK: FOR THIS A VERY LOW INTERFACIAL VISCOSITY IS DESIRABLE

Fig. 11- Schematic diagram of the role of low interfacial viscosity in the surfactant (9) flooding process.



COALESCENCE OF OIL GANGLIA WITH OIL BANK CAUSES FURTHER DISPLACEMENT OF OIL

Fig. 12- Schematic diagram of the role of coalescence of oil ganglia in the surfactant (9) flooding process.

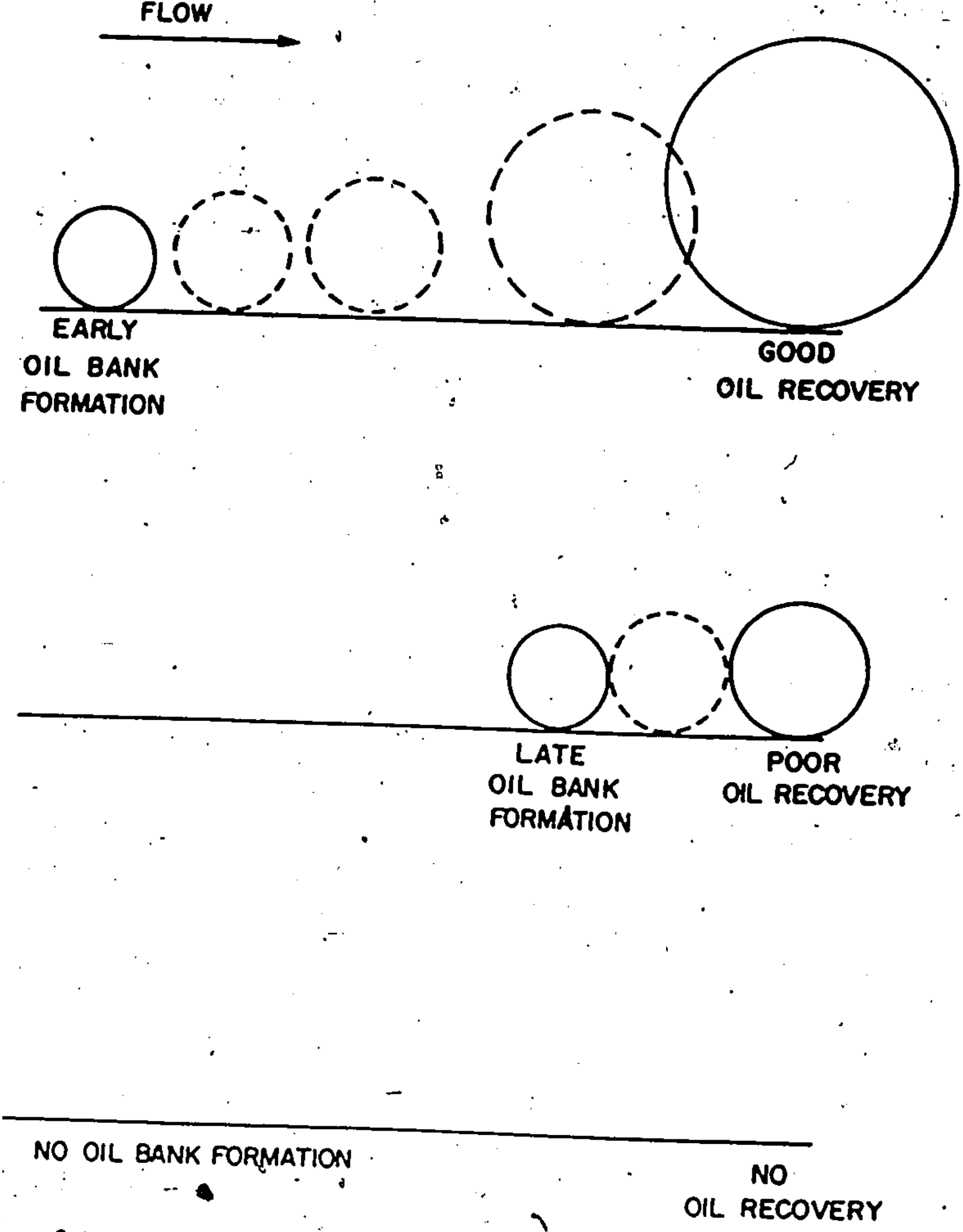


Fig. 13 - Schematic illustration of the injection of an oil bank and the subsequent "snowball effect" in enhanced oil recovery. (49)

It has been known for some time that the capillary forces are the major contributors in trapping the residual oil in the porous medium. The "doublet" model is a very good way to explain the mechanisms involved (10).

Melrose and Brandner (11) have shown that the trapped oil will mobilize only if the capillary forces are the dominant ones during the displacement process. In other words, to mobilize the trapped oil, a dimensionless ratio called "the capillary number (N_{ca})" has to exceed a critical value. This number represents the ratio of viscous to capillary forces, thus;

$$N_{ca} = \frac{\mu \, V}{\gamma \, \phi \, \mathrm{Cos}\,\theta} \qquad (7)$$

where μ and V are the viscosity and mean velocity of the displacing fluid, γ is the interfacial tension and ϕ and θ are the porosity and contact angle respectively. In an attempt to better understand the oil displacement process Taber (8) recently summarized the many empirical numbers proposed by previous investigators. Figure (14), which has been reported by Foster (12), depicts such a typical correlation between the capillary number and the residual oil saturation .

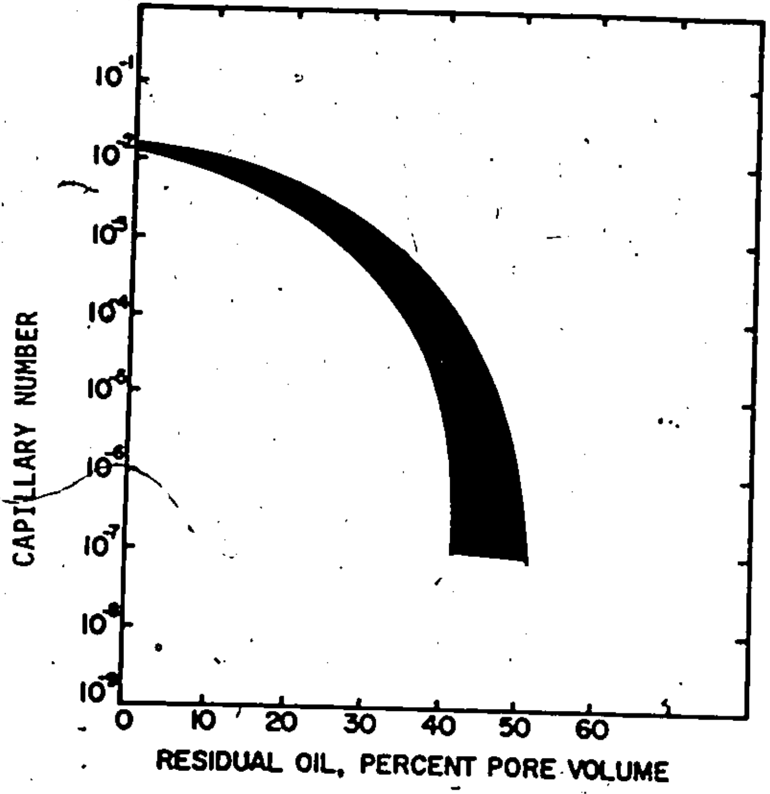


Fig. 14- Dependence of residual oil saturation on Capillary Number (Foster, W.R., J. Pet. Tech., p. 206, Feb. 1973). (9)

At the end of waterflooding, the capillary number is typically about 10^{-6}. As indicated by Figure (14), for residual oil to be mobilized, this number has to be increased to $10^{-4}-10^{-2}$. For a good recovery, N_{ca} has to be greater than 10^{-3}. This can be achieved by reducing the IFT in the reservoir from the typical 20-30 mN/m range to $10^{-3} - 10^{-4}$ mN/m .

Ionic Strength

Ionic strength represents the combined effect of valency and ion concentration, and is defined by :

$$IS = (1/2)\sum_{1}^{i} c_i Z_i^2 \qquad (8)$$

Where,

c_i = Molar concentration of the ith ionic species
Z_i = Valency of the ith ionic species

This parameter has been known to affect the electrolytic properties and IFT behavior of the connate water against crude oil. Increasing the ionic strength increases the shielding of the surfactant ions, thereby decreasing their Coulombic repulsion energy (8).

Optimum Salinity

Oil/brine/surfactant systems often form "middle-phase" microemulsions in an appropriate salinity range. The salinity at which this middle phase contains an equal volume of oil and brine is called the "optimum salinity" (9).

At optimum salinity the interfacial tension is minimum and, therefore, the oil recovery would be expected to be maximum (Fig. 15). Divalent cations have been known to affect the optimum salinity by increasing the oil-water IFT in the presence of surfactants.

Surfactants Properties

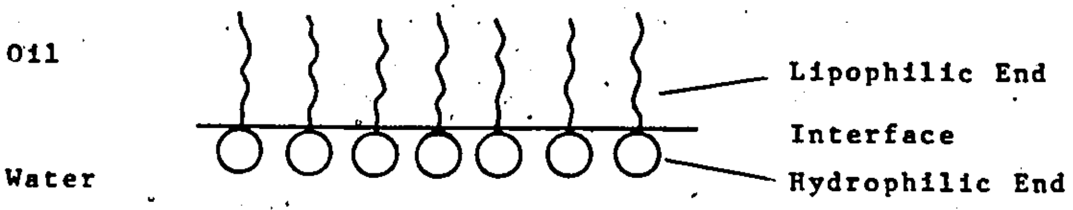
Surface active agents possess both polar and non-polar regions on the same molecule. The polar (hydrophilic) region of the molecule may carry a positive or negative charge (cationic or anionic surfactants) or may be composed of polyoxyethelene chains (non-ionic surfactants). The petroleum sulfonates used in this research are anionic surfactants.

Surfactant Adsorption

Reservoir clays have high adsorption capacities which result in serious surfactant retention. This loss of expensive surfactants due to adsorption is considered to be one of the major economic limitations of surfactant flooding processes. Increasing the amount of electrolyte will increase the surfactant adsorption. Trogus et al (38) found that for anionic surfactants (such as the petroleum sulfonate P-420 used in this research) adsorption increases with molecular weight, while for non-ionics the opposite is the case.

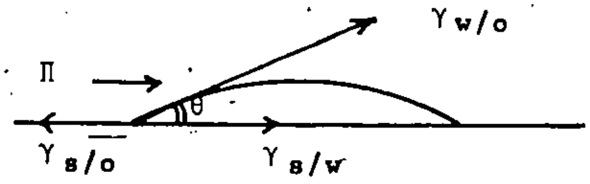
The Phenomenon of Fingering

If the mobility of the displacing phase (usually water) is greater than that of the displaced fluid (oil), in other words if $M > 1$, the displacing fluid will by-pass portions of the reservoir and will not contact all of the oil. This phenomenon is called "viscous fingering", and is one of the biggest problems encountered in enhanced oil recovery. In general, the lower the mobility ratio, the better the sweep efficiency. Mobility ratios of greater than five ($M > 5$) are not ideal in EOR.



$$\Pi = \gamma_{s/o} - \gamma_{s/w} \qquad (9)$$

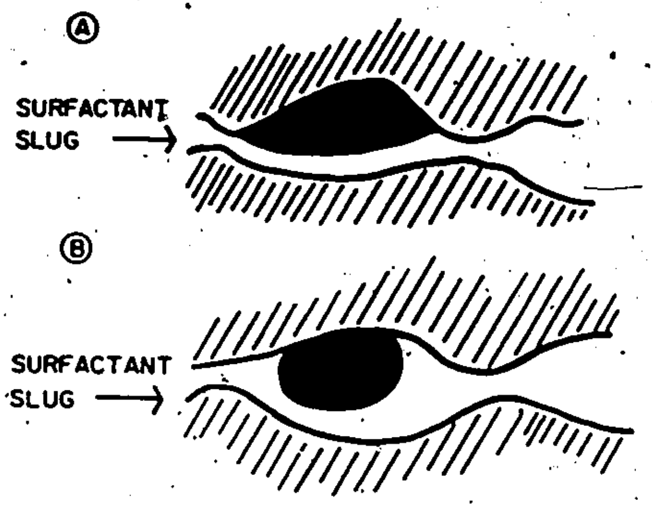
Π = Surface Pressure of the Adsorbed Film



$$\cos\theta = \frac{(\gamma_{s/w} - \Pi) - \gamma_{s/w}}{\gamma_{w/o}} \qquad (10)$$

If Cos θ decreases, θ will increase and so will Π ; This would result in a less water-wet medium.

Fig. 15 - Surface Pressure and Adsorption



PROPER CHOICE OF SURFACTANT CAN CHANGE Ⓐ TO Ⓑ

Fig. 16 -The role of wettability and contact angle on oil displacement. (9)

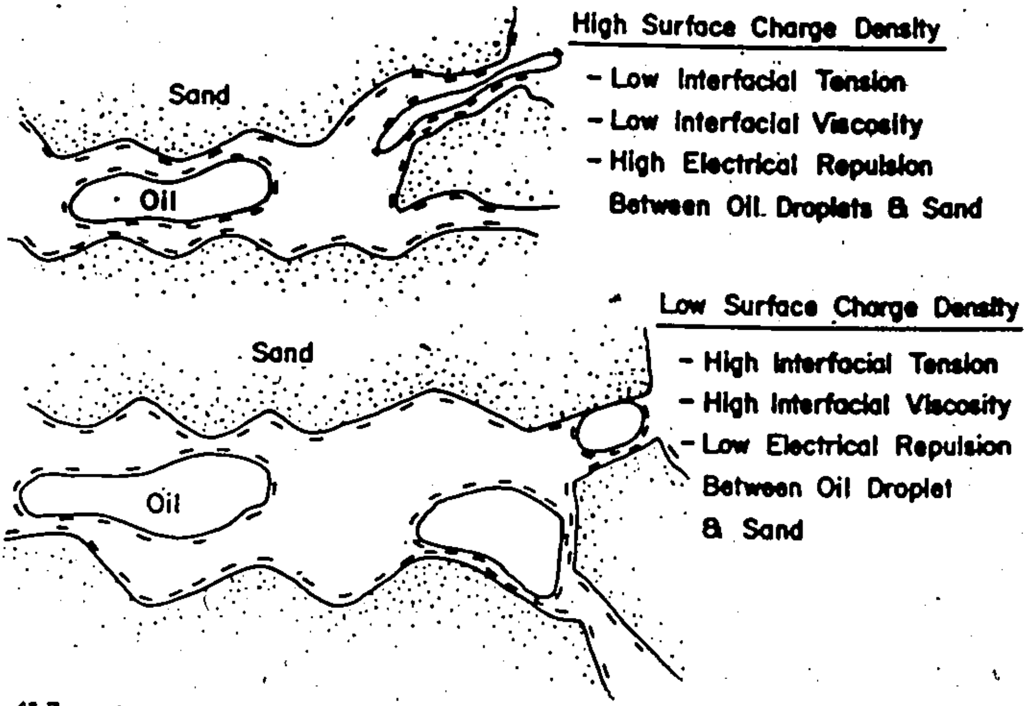


Fig. 17. Schematic diagram of the role of surface charge in the oil displacement process. (9)

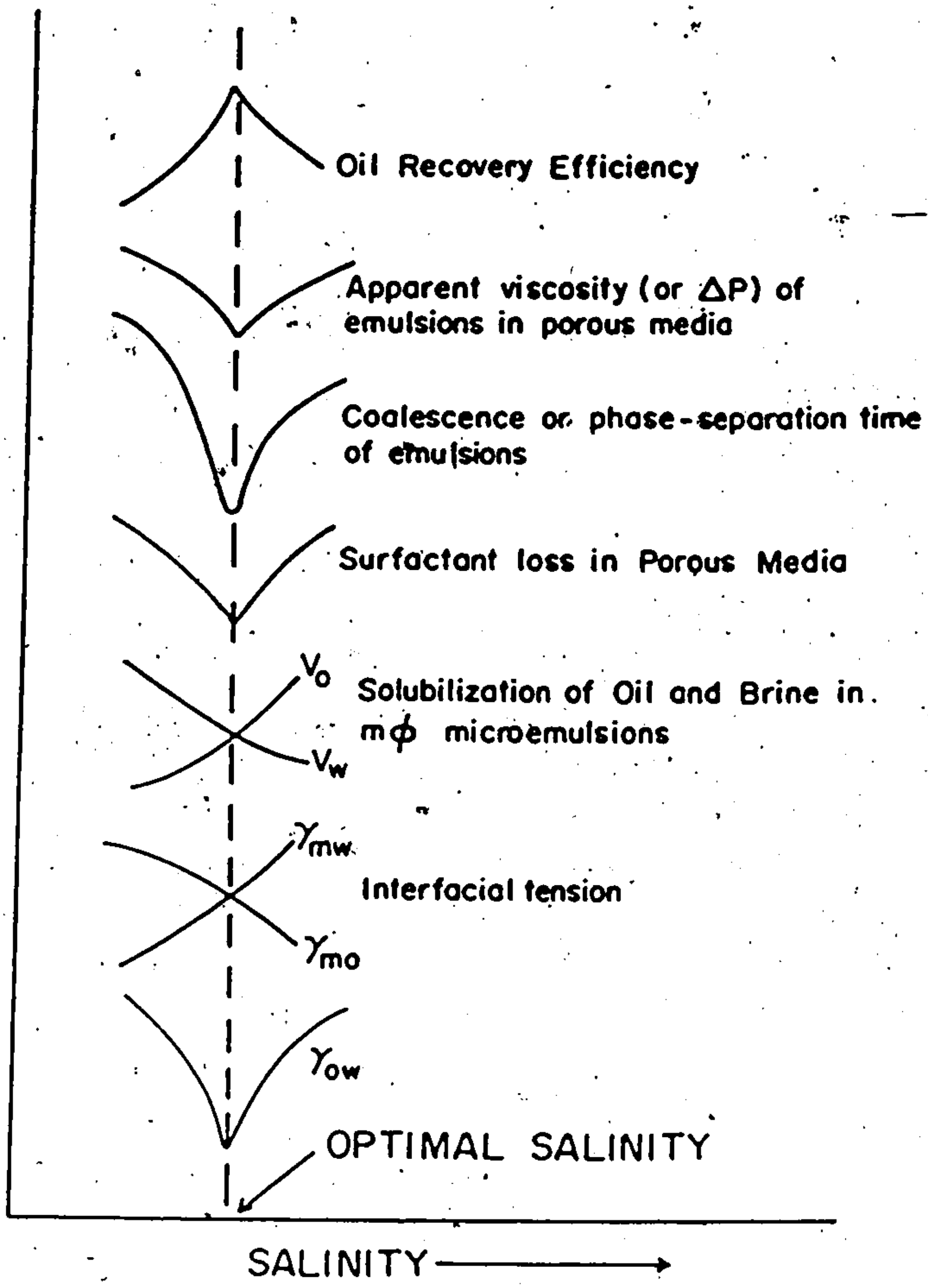


Fig. 18- A summary of various phenomena occurring at the optimal salinity in relation to enhanced oil recovery by surfactant-polymer flooding. (9)

1.5- The Potential of EOR

It has been estimated that 5-10 percent of the 640 billion cubic meters (1. m^3 6.29 barrels) of the OOIP in the world is recoverable by EOR; making it as important as exploring for new discoveries (Table 2). In Canada, EOR will add $636 * 10^6$ m^3 or 64% to the nation's remaining established light and heavy crude oil reserves of one billion cubic meters. Only about 30% of the light and medium and less than 10% of the heavy OOIP is recovered by primary and secondary recoveries. For the remaining 70 to 90 percent, EOR methods have to be employed (2).

In 1980, about 40 percent of the total oil produced in the United States, was recovered using EOR methods (including water flooding). In 1984, EOR production in Canada was 74,400 b/d up 5% from the previous year. Hydrocarbon miscible contributed 82.4% and steam 16.7% with 12,400 b/d (13).

Since EOR processes are high risk ventures, the level of activity will be related to the extent that business climate fosters such activity. Generous tax and royalty incentives are expected to spur additional EOR project activity; that is if the international oil prices do not remain at the present low level for long periods of time.

Table 2- Estimates of EOR production (2).(1979)

(cubic meter per day)

Methods	World	United States	Canada
Steam	64,400	47,000	1,500
In Situ Combustion	8,700	1,900	1,100
Miscible		11,900	1,200
Chemical		400	
Others	35,100		
Total	108,200	61,200	3,800

CHAPTER II

LITERATURE SURVEY

The first deliberate attempt to produce oil from underground reservoirs by the injection of aqueous fluids may have occurred in Sweden before 1740. At that time, running water was used to force crude oil out of rocks containing tar sands (14).

In the USA, early operators believed that injection of water into oil reservoirs would "drown" the oil wells. In fact, the laws of many States actually prohibited injection of water into the productive zones. However, by the middle of the nineteenth century, the situation had changed and water-flooding was considered an excellent method for increasing oil production . In 1917, Squires (15) concluded that addition of an alkali into the water would improve the oil displacement and he managed to acquire the first patent to use caustic solutions in oil recovery.

By the mid-1920's, engineers were already doing research on how to reduce the interfacial forces which are responsible for holding the oil in the reservoir rock, in order to increase the recovery.

Uren and Fahmy (17) did important work investigating the effect of various "factors" which would influence the oil recovery, the results of which are still valid today, some 60 years later. One of their major achievements was to suggest that the interfacial forces far exceed the viscous forces in the porous medium and that the capillary forces are primarily responsible for the holding of the oil in the reservoir rock.

The trapping of the residual oil by the capillary forces has been explained by Beuner and Bartell's pore doublet model (Fig. 19) for a water-wet reservoir (i.e., contact angle <<90). In this model pores are represented by two parallel capillaries of equal length initially saturated with oil . If the imbibition rate is greater than the displacement velocity, as in most flooding cases in the field, the injected fluid will travel faster through the smaller capillary. As soon as the displacing fluid reaches the point of convergence of the two pores, the recovery from the larger pore will cease and consequently some oil will remain trapped inside that pore (18).

In 1936, Wyckoff and Botset (16) did the first reliable experiments on relative permeability and observed that a specific minimum saturation is an essential condition for the flow of oil in the porous medium. Meanwhile, researchers had proved that the discontinuity of the oil phase was a major problem in oil recovery.

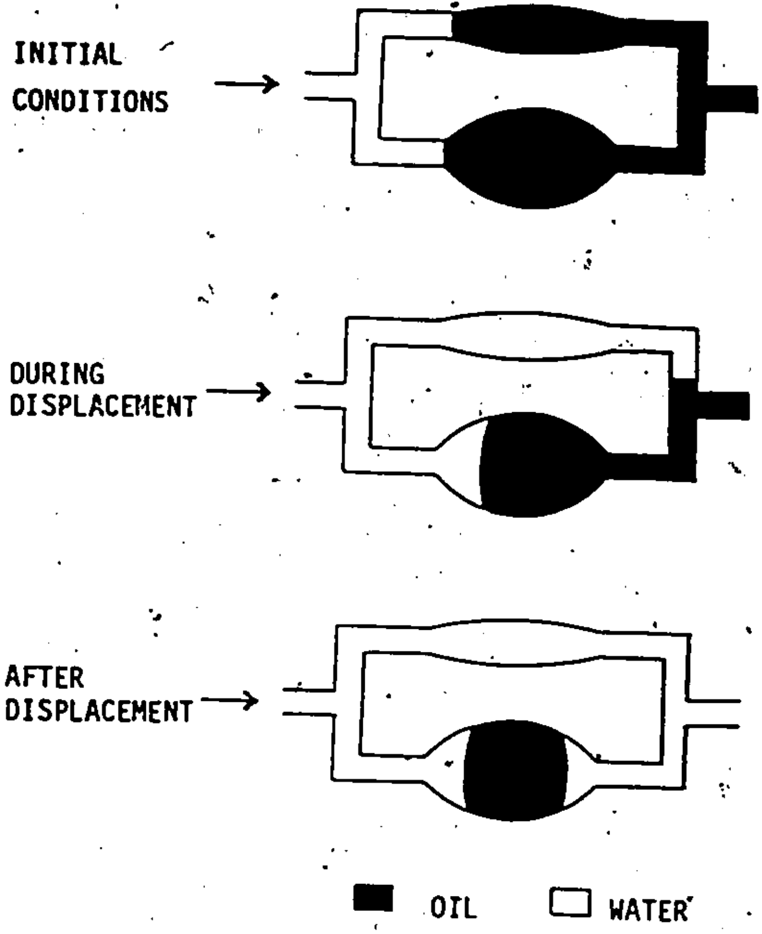


FIG. 19- STRANDING OF RESIDUAL OIL

The methods for altering the surface forces and thereby improving oil recovery may be classified into three often interacting areas. They consist of changing :

1) The wettability
2) The oil-water interfacial tension
3) The interface (miscible flooding)

2.1- Wettability

Taber (8) has compared the wettability to the weather. For years everybody talked but until recently nobody did anything about it. In 1860, Jamin (19) noted that a series of gas bubbles in a smooth capillary tube could create large resistances to flow. This effect is dependent upon the advancing and receding contact angles (measured through the aqueous phase). In other words, preferential wetting is essential to the existence of capillary forces.

Since the majority of the porous media are extremely complex systems, it has been very difficult to study the direct effects of wettability on oil recovery. It is almost impossible to measure the contact angle in a porous medium made up of various minerals and with particles of different shapes and sizes. Considering the high energy surfaces of the reservoir rock, this task becomes even more difficult.

In 1938, Bartell et al noted that for many crude oils the receding contact angles were always less than 90 degrees (indicating a water-wet system), and the advancing contact angles were considerably greater than 90 degrees (oil-wet systems). Clearly, in such cases, neither the oil nor the water can advance into a pore by capillary forces alone (non-imbibition). They therefore concluded that for any spontaneous displacement of oil by water, both the advancing and receding contact angles must be less than 90 degrees.

Morrow (20) found that for systems which imbibe, the highest recovery should be obtained with strongly water-wet systems. Earlier, in 1956, Moore and Slobod (21) had experimentally proved that the capillary forces in strongly water-wet systems were responsible for trapping of oil in larger pore spaces and almost none of this residual oil could be produced after water breakthrough at any reasonable flooding rate (permanently trapped residual oil).

Various researchers have tried to improve oil recovery by changing the wettability properties of the reservoir . As mentioned earlier, Squires (15) obtained a patent involving addition of alkaline materials. Then, in 1928, Nutting (46) suggested the addition of sodium carbonate and silicates to the flooding fluid. In 1956, Reisberg and Doscher (22) added sodium hydroxide to the water and observed increased recovery. Later in 1959, Wagner and Leach (23) proved that a drastic change in the pH of the water could turn an oil-wet rock into a water-wet one and therefore increase the recovery.

One of the most successful field experiments was carried out in 1974 by Graue and Johnson (24) and is called "the emulsification and entrapment" method. It involved the emulsification of much of the oil (rather than a wettability change) and thereby partial blocking of the flow of water in some areas, consequently leading to an increase in the overall sweep efficiency.

2.2- Surfactant and IFT

One of the biggest setbacks of flooding using surfactants has been their loss by adsorption onto the large surface area of the rock. From the economics point of view this can prove disastrous, while technically it prevents the advance of the surfactant with the fluid through the rock formation. Taber (25) noted in lab tests that increasing the surfactant concentration to about 10%, largely eliminated this problem, although this subsequently proved to be inconsistent with actual field recovery results. While performing these experiments he found that the most sensitive variable in surfactant flooding was the displacement velocity.

He concluded that the above inconsistency would no longer exist if all experiments were carried out at equivalent values of the ratio of viscous to interfacial forces, i.e. at equal values of the capillary number, N_{ca}.

Several people have described mechanisms responsible for surfactant retention including adsorption, precipitation, partitioning into residual oil phase and entrapment of immiscible microemulsion phase. Glover et al (42) discovered that if retention is excessive, IFT will eventually become high enough to entrap residual oil in the reminder of the reservoir.

In 1926, Harkins and Zollman (28) reported that the addition of electrolytes to the surfactant system reduced the oil-water interfacial tension. Later, Reed and Healy (47) developed the concept of optimal salinity. In 1979, Hwan and Miller (29) proved the existence of water in oil micro emulsions at high salinities and oil-in-water microemulsions at lower salinities. Glover et al (42) reported that divalent ions would form sulfonate species which could strongly influence the microemulsion phase behavior. They have suggested a useful method of predicting phase behavior in systems containing divalent ions. This method combines equilibrium expressions that describe sulfonate-cation association with a relationship defining the contribution of each surfactant component to optimal salinity.

In the past twenty years, much work has been done in the area of oil recovery by microemulsions (micellar fluids). To prevent possible fingering of the displacing phase into the displaced phase, it is necessary to have good mobility control. This can be achieved by increasing the viscosity of the displacing microemulsion. Usually a water soluble polymer is added to the drive water (mobility buffer). To prevent the adverse effect of polymer-surfactant interactions (phase separation, surfactant entrapment), a cosurfactant such as an alcohol is added to the solution.

In 1977, Cayias (26) showed that when measuring the IFT of pure hydrocarbons against a surfactant solution, the minimum IFT was obtained against only one of the hydrocarbons in any given homologous series. This minimum IFT is very specific and is general for all kinds of hydrocarbons. Subsequently Cash et al (27) assigned an "equivalent alkane carbon number" (EACN) to pure hydrocarbons, and to mixtures such as crude oil. For most crude oils the EACN is between 6.2 and 8.6. This knowledge permits researchers to work with pure hydrocarbons instead of with crude oil, yet still be confident that their results will not significantly differ from those for crude oil. Later they developed the concept of an n_{min} value (i.e., the specific EACN which produces the lowest IFT for a given surfactant). This parameter proves to be very useful when studying the effects of such variables as electrolyte concentration, temperature, system age and surfactant concentration (e.g. n_{min} decreases with temperature and increases with electrolyte concentration.

2.3- Changing the Interface (Miscible Flooding)

No matter how good the displacement conditions, there will always be some trapping of oil in the smaller capillaries. In theory, only part of this residual oil is recoverable by waterflooding alone. However, if the flooding fluid is miscible with the oil, there is the possibility of producing much larger amounts of the entrapped oil. Since there is no clear interface in the case of miscible flooding, capillary forces will no longer be effective, and the dynamic and viscous forces are then able to push the residual oil out of the rock formation.

2.4- Past Research On Divalent Ions

Most previous researchers have studied the IFT and recovery behavior of surfactants in the presence of Na^+ and Cl^- ions only. However, actual reservoir connate waters often contain other monovalent ions as well as some divalent ions such as Ca^{++} and Mg^{++}.

In 1974, Jennings (31) and Cooke (32) reported that the presence of Ca^{++} and Mg^{++} ions drastically increases the oil-water interfacial tension. To obtain a fundamental understanding of EOR mechanisms, the effects of connate water composition must be taken into consideration. With this in mind, Dranchuk et al (36) used original field connate water in their displacement tests. Bansal and Shah (30) discovered that there is an increase in IFT and solubilization upon increasing the $CaCl_2$ (or $MgCl_2$) concentration in the connate water. They also noted that the optimal salinity decreases upon increasing the concentration of divalent cations. This increase was more drastic in the case of Ca^{++} than with Mg^{++} ions. In a related study, Hirasaki and Lawson (37) studied the association of sodium and calcium ions with surfactant micelles using electrostatic and equilibrium models.

Hirasaki (41) found that the effect of divalent ions on optimal salinity could be expressed as a linear function of the divalent ion fraction of the total cations associated with the surfactant. Bansal and Shah (30) reported a decrease of the optimal salinity upon introduction and increase of the amount of $CaCl_2$ in the surfactant formulation. In other words, those surfactant formulations were capable of producing very low IFT at optimal salinity value in the presence of high concentration of divalent ions. In addition calcium ions seemed more effective in lowering optimal salinity as compared to magnesium ions.

Celik et al (40) reported complex behavior of multivalent ions involving precipitation followed by redissolution of the precipitates at higher surfactant concentrations. They believe that the formation of micelles capable of solubilizing the precipitated sulfonate is a detrimental factor in the redissolution process. They have suggested addition of NaCl to the divalent ions solution as a salinity control to reduce or prevent the precipitation formation caused by multivalent ions. They showed that redissolution is mainly caused by micelles. This involves uptake of calcium by the micelle followed by redissolution of the precipitate to replenish the system with calcium ions and the formation of additional micelles by the released sulfonate.

In another paper, Bansal and Shah (43) have suggested that petroleum sulfonate solutions have very poor salt tolerance (i.e. precipitation occurs at very low salt concentrations). However, upon further increase in salt concentration, the precipitate redissolves in the solution and a stable birefrigent phase forms. A further increase in salt concentration will destroy this birefrigent phase and will result in phase separation. Addition of Ethoxylated sulfonate (EOR-200) into petroleum sulfonate will remarkably increase the salt tolerance of petroleum sulfonate solutions (a synergistic effect of blending). Several other workers have proposed mechanisms of redissolution of precipitate. They can be generalized as : premicellar complexation, redispersion of the coagulated precipitates and micellar solubilization.

Kumar et al (33) carried out experiments with dilute surfactant formulations. They found that for solutions containing calcium chloride and magnesium chloride, an increase in the sodium chloride concentration does not significantly affect the IFT behavior, while an increase in the amount of calcium chloride or magnesium chloride considerably increases the IFT.

Divalent ions have been known to cause a number of complications during the various EOR processes. For example, they could deplete an alkali slug by the formation of insoluble hydroxides (during caustic flooding processes). This could be avoided by introducing a fresh water or sodium chloride buffer before injection of the alkali. Similarly, during flooding with surfactants, the surfactant and divalent ions often form a precipitate which may or may not hinder the oil recovery process.

2.5- Objectives of the Present Work

The present study is concerned with the effects which divalent ions have on the behavior of such important parameters as the oil-water interfacial tension, the ionic strength, the capillary number and, finally, the oil recovery itself. The principal objective has been to elucidate the relationships between the existence of divalent ions in connate water on the one hand, and all of the above factors on the other. Serious efforts have been made towards proposing fundamental mechanisms to explain the experimental observations. However, it should be noted that the purpose of this research project has not in any way been to maximize or optimize the recovery process itself.

PART II

EXPERIMENTAL METHODS

CHAPTER III

FORMULATION AND CHARACTERISTICS OF CRUDE OIL, SAND, SURFACTANT AND CONNATE WATER

3.1-Crude Oil

The crude oil selected for this study was a light crude from Chatham, Ontario. This crude was preferred over some other oils such as Lloydminster or Cold Lake heavy oils mainly because, as Chiwetelu (34) has described, the use of these oils would bring about several difficulties resulting in poor recovery. On the other hand, the Chatham oil had already been analyzed upon our department's request by Petroleum and Gas Laboratories of Canada Center for Mineral and Energy Technology (Table 3).

3.2-Porous Medium

The porous medium was made of glass beads (Flex O Lite,BT 12) manufactured by Ritchey Supply Limited (Table 4).
The sand was first sieved through sieves No. 100 and 230. By reducing the size distribution range we hoped to produce a more homogeneous medium and thereby improve the reproducibility of the results. Under a high power microscope all the particles were observed to have spherical shapes.

Table 3-Properties of Chatham Crude Oil

Density at 25°C (g/cm^3)	0.824
API Gravity at 60°F	39.4
Viscosity at 25°C (cp)	5.55
pH	5.8
Color	Greenish Black
Carbon, % by weight	85.70
Hydrogen, % by weight	13.39
Nitrogen, % by weight	0.40
Sulfur, % by weight	0.18
Ash, % by weight	0.007
Water, % by weight	Nil

Table 4-Characteristics of the Porous Medium

Permeability K, ($\mu m)^2$	1-2
Porosity ϕ	0.34-0.36
Bead Density d, (g/cm^3)	2.50
Particle Diameter D_p, (μm)	63-149

3.3-The Surfactant

The surfactant used in this research project was a petroleum sulfonate commercially known as Petrostep-420 manufactured and marketed by Stepan Chemical Company of Northfield, Illinois. The properties of this surfactant are summarized in Table 5.

Table 5-Specifications of Petrostep-420

Approximate Equivalent Weight	420
Active Sulfonate content, % by Weight	59.1
Free Oil, % by weight	17.3
Water, % by weight	19.5
Inorganic Salts, % by weight	4.1

As was earlier mentioned (9), in order to obtain minimum IFT the experiments have to be carried out at around the optimal salinity. For a system of 0.2% P-420 and sodium chloride this happens at a concentration of 1.5 % by weight (Fig. 20). To make the surfactant solution compatible with the connate water, first an aqueous solution of 1.5 % (wt) sodium chloride was prepared. Then the desired amount of surfactant was added to it. The solution was stirred until all of the P-420 was completely dissolved (a period of 24 hours). This procedure

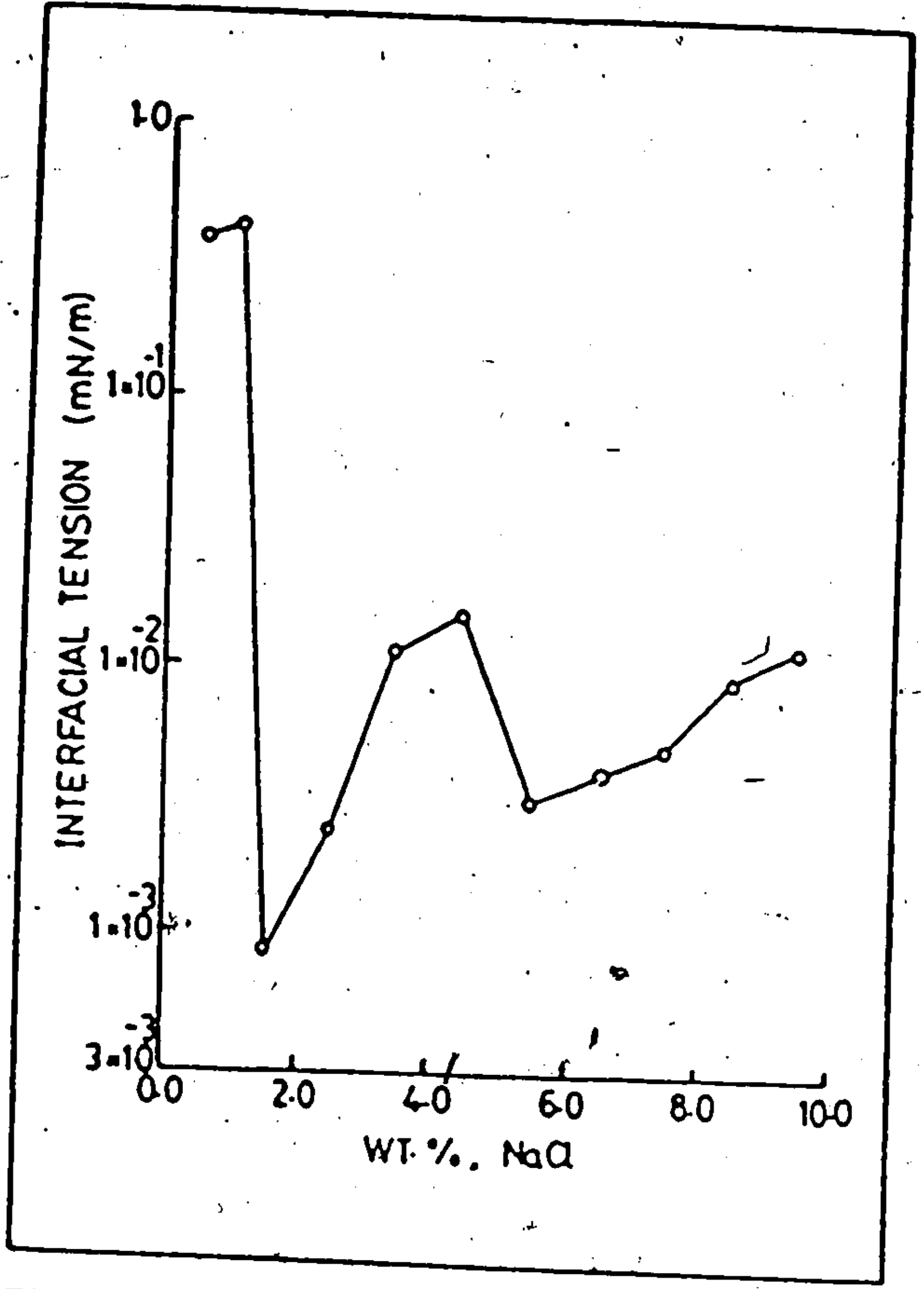


Fig. 20- Effect of sodium chloride concentration on interfacial tension.(5)

would eliminate all the possible problems such as the precipitate formation due to high concentration of salt in some regions of the solution. As we will see later it was found that the surfactant solutions would lose their IFT reduction effect after some time. Therefore, in order to have reproducible results, it was decided to use fresh surfactant solutions.

3.4-Connate Water

High purity sodium, magnesium and calcium chlorides provided by Fisher Scientific Company were used in this project. The solutions were all prepared in the same identical manner using distilled water.

Hexadecyl Trimethyl Ammonium Bromide (HDTB) was used as an emulsion breaking agent (57).

CHAPTER IV

IFT, pH AND VISCOSITY MEASUREMENTS

4.1-IFT Measurements

IFT measurements were carried out using a University of Texas spinning drop tensiometer. A detailed description of this method has been given by Cayias et al (39). A standard capillary tube is filled up with the connate water and then a small droplet of crude oil is introduced. The cell is placed in a slot on a shaft of a rotor assembly. It is spun for 1-6 hours (sometimes longer) at speeds ranging from 1200-24000 rpm. Keeping the temperature constant at 25°C, the droplet width is measured at constant intervals until an equilibrium is reached. To calculate the IFT the following formula is used :

$$\gamma = 0.522 \, \Delta\rho \, (d^{3} / T^{2}) \qquad \textbf{(11)}$$

Where :

γ = Interfacial tension mN/m

$\Delta\rho$ = Density difference between the oil and water

d = The diameter of the droplet

T = The inverse of the angular velocity

Gravity measurements were made using a 25 ml specific gravity bottle at room temperature of 24 ± 1 °C.

4.2-pH Measurements

These measurements were conducted using a Beckman Zeromatic SS-3 pH-meter and Fisher standard combination electrode. To adjust the instrument, pH buffer solutions of 4 and 7 (also provided by Fisher Sci. Co.) were used prior to each measurement. During the experiment the room temperature of 24 ± 1 °C prevailed.

4.3-Viscosity Measurements

The viscosity was measured using a Brookfield viscometer with a U.L. adapter (provided by Brookfield Engineering Laboratories). This viscometer operates by measuring the torque necessary to overcome the viscous resistance to the induced movement. The accuracy of this viscometer is about 1 2% of the full scale range employed. Sixteen ml of the solution was placed in the stainless steel tube of the U.L. adapter and then the precision cylindrical spindle was introduced into the cylinder. This assembly was then attached to the viscometer. The measurements were taken after equilibrium was reached.

CHAPTER V

EXPERIMENTAL PROCEDURES

5.1-Apparatus

Figure (21) provides details of the oil displacement apparatus. The system specifications are as follows :

The Core Holder :

Length (L)	43.2 cm
Cross sectional area (A)	12.1 cm^2
Inside diameter (I.D.)	3.8-3.9 cm
Volume (V)	523 cm^3

Inside Diameter of the Pipe	0.683 cm
Nominal Diameter	1/8 inch

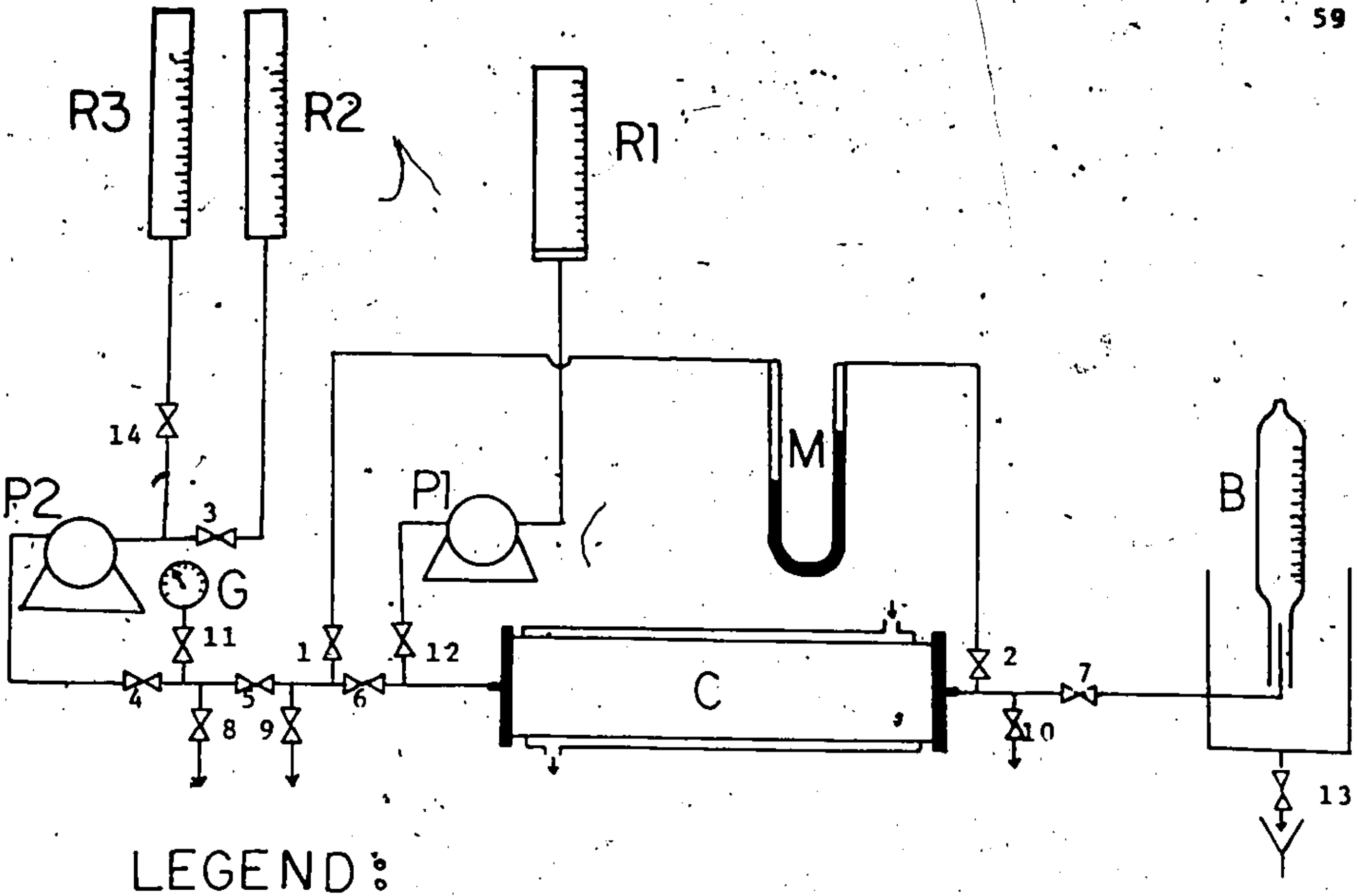
The Pumps :

1) Crude oil pump details are given by Bansal (5).

2) Connate water-surfactant pump was a Beckman model 110-A pump capable of pumping 0.1 to 10 ml per minute in 0.1 ml per minute increments.

Flanges :

The details of the flanges are given in Fig.(22).



LEGEND:

B : REVERSED BURETTE FILLED WITH WATER

C : CORE HOLDER (CELL)

G : UPSTREAM PRESSURE GAUGE

M : DIFFERENTIAL PRESSURE MANOMETER

P1 : OIL INJECTION PUMP

P2 : BRINE-SURFACTANT INJECTION PUMP

R1 : CRUDE OIL RESERVOIR

R2 : SURFACTANT RESERVOIR

R3 : BRINE RESERVOIR

Fig. 21 - Oil Displacement Apparatus

5.2-Cell Packing and Preparation

The "Wet Packing" method was used to prepare the core holder. The cell was first filled with the appropriate amount of a connate water and assembled onto a vibrator. The glass beads were then weighed and poured into the cell through a funnel with an adjustable valve (Fig. 23). This would permit a uniform rate of sand discharge into the core holder and would also prevent the formation of air bubbles. After the core holder was packed with sand, it was left on the vibrator for several hours until it was certain that the porosity could not be further reduced. The second flange was then attached to the cell. As can be seen in Fig. (22), The fiberglass in the hollow part and also the frit would ensure a uniform injection of oil or the surfactant from the total cross-sectional area of the flanges and at the same time would reduce the dead volume to about 2 ml in each flange.

After the sand packing process was completed, the core holder was assembled on the displacement apparatus and permeability measurements were initiated. To calculate the permeability of the porous medium, the pressure drop along the core was measured for different flow rates of the same connate water originally in the cell. Then, according to Darcy's law, a graph of (Q/A) vs. ($\triangle$P/L) was plotted (Fig.24). A computer was then used to obtain the best fitting line through those

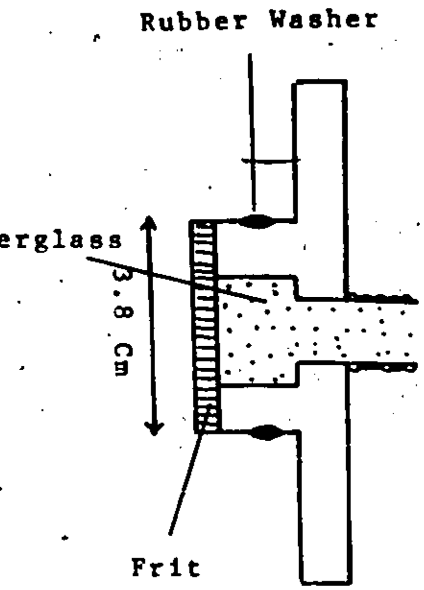


Fig. 22 - Details of the Flanges

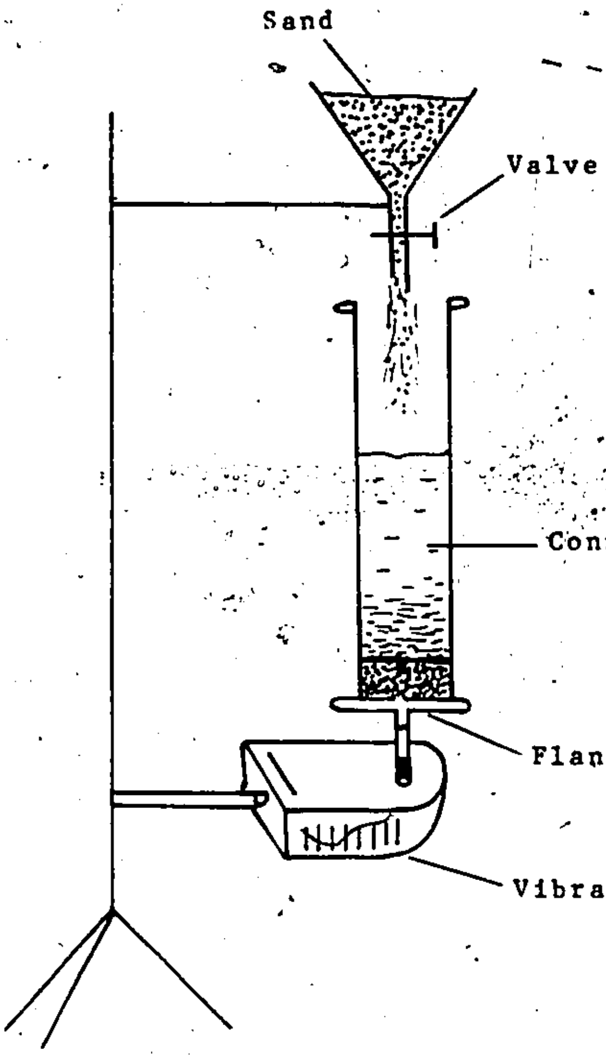


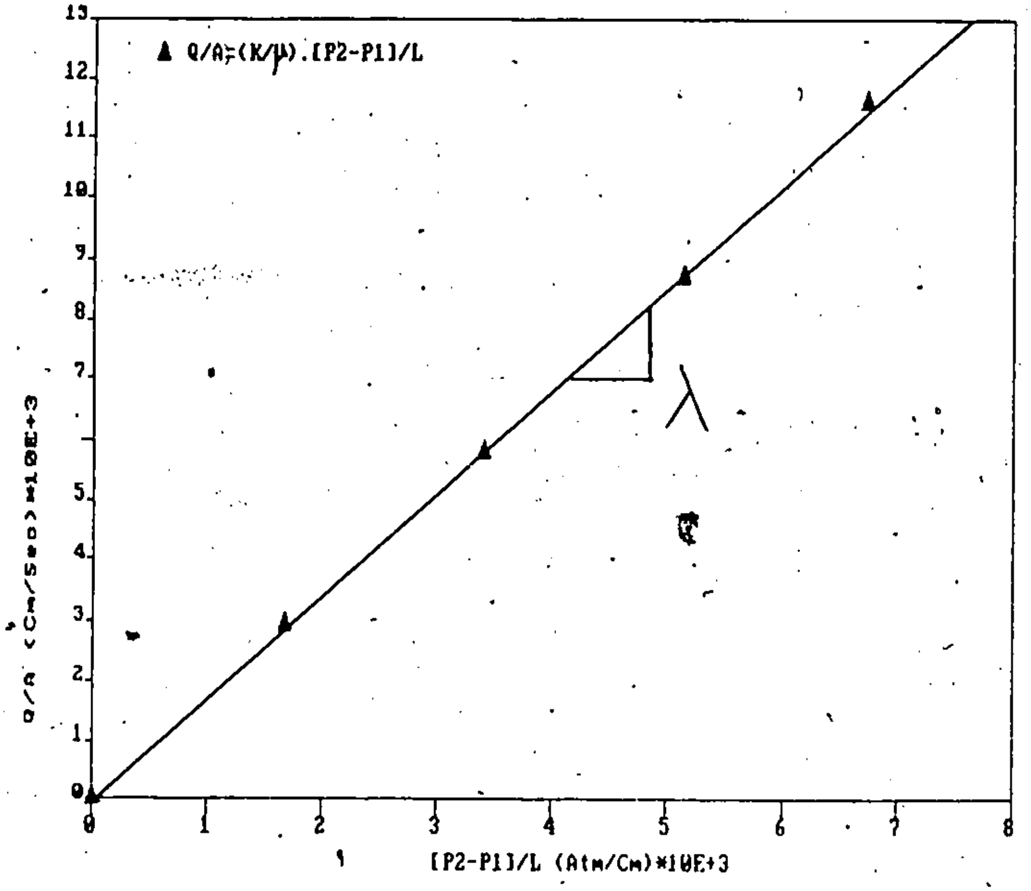
Fig. 23 - Wet Packing

DARCY'S LAW

$$\frac{Q}{A} = \lambda \cdot \frac{\Delta P}{L}$$

$$\lambda = \frac{K}{\mu}$$

Fig. 24 - MOBILITY MEASUREMENT FOR RUN NO. : 23



points (linear regression) and calculate the slope of the line which would give the mobility (M). Having the viscosity of the fluid, the permeability of the porous medium (K), could be easily calculated.

5.3 Flooding Strategies

The displacement experiments were conducted using two strategies.

Strategy I

1) Secondary Recovery : The porous medium was flooded with 5-6 pore volumes of a brine having the same composition as the connate water originally in the cell until no more oil could be recovered. Since the oil is recovered by dynamic and viscous forces, this part of the displacement is a purely physical process at the end of which a large part of the oil has been recovered and the pore space is filled primarily (60-70%) with brine and of course some still unrecovered oil. The cell preparation and secondary recovery usually took about 10 hours.

2) Tertiary Recovery : The following day, 3-4 pore volumes of the surfactant solution were injected into the porous medium until the irreducible oil saturation (S_{oir}), was reached. In this process the oil is recovered both by chemical forces

caused by interactions of surfactant, connate water and oil, as well as by viscous and dynamic forces produced by the flow.

Strategy II

This strategy did not involve brine (connate water) flooding. The core was immediately flooded with 5-6 pore volumes of the surfactant solution. This could be considered both a physical as well as a chemical process. Strategy II took about 10 hours to complete.

A major difference between the two strategies is that in the beginning of Strategy II, the surfactant solution comes in contact with a porous medium containing only about 10% connate water and 90% oil, while during Strategy I the brine forms about 60-70% of the pore volume.

5.4-Flooding Procedure and Recovery Analysis

An appropriate amount of glass beads was weighed. Having the solid bead density, its volume was then calculated. As mentioned earlier, the cell was then packed with the glass beads using the wet-packing method. Furthermore, the porosity and pore volume of the medium were calculated. The pipes were rinsed and cleaned with a flush of connate water using pump P2 (Fig.21). The core holder was then assembled onto the apparatus. Attention was paid so that no air bubbles could get into the system. The valves 3, 8, 9, 10, 11 and 12 were closed and pump P2 turned on. Using manometer M and flow rates of 2, 4, 6 and 8 ml per minute the pressure drop through the porous medium was measured at equilibrium. This enabled us to calculate the mobility of the fluid used and the permeability of the porous medium. Pump P2 was then shut off and valves 1, 2 and 13 were closed. Burette B was filled with water and a 1% (wt) solution of the emulsion breaking agent HDTB and it was then reversed on the outlet pipe as shown in Fig.(24). Valve 12 was opened and pump P1 turned on at 25% stroke-length (7.23 ml/min). An appropriate amount of oil was injected into the porous medium and extra amounts leaving the outlet were recovered in burette B and measured. Assuming the oil to be an incompressible fluid (reasonable for our purposes), the initial oil saturation could be easily calculated by a simple mass balance. The burette was then cleaned and filled with some fresh water and solution of HDTB. We were now ready for secondary or pseudo-secondary (Strategy II, using surfactants without prior water flooding) recoveries.

The valves 1, 2, 3 or 14, 8, 9, 10 and 12 were kept closed and all others open. Depending on the strategy employed, the brine (connate water) or surfactant were injected at a constant rate of 4 ml per minute. The oil recovered in the burette was measured at 500 second intervals until no more could be recovered.

In the case of strategy I, valve 13 was then closed and valve 3 opened. The surfactant solution was injected into the porous medium and the corresponding recovered oil was measured in burette B.

PART III

EXPERIMENTAL DATA ANALYSIS

AND

DISCUSSION OF THE RESULTS

CHAPTER VI

INTERFACIAL TENSION AND CONTACT ANGLE MEASUREMENTS

6.1-IFT STUDY

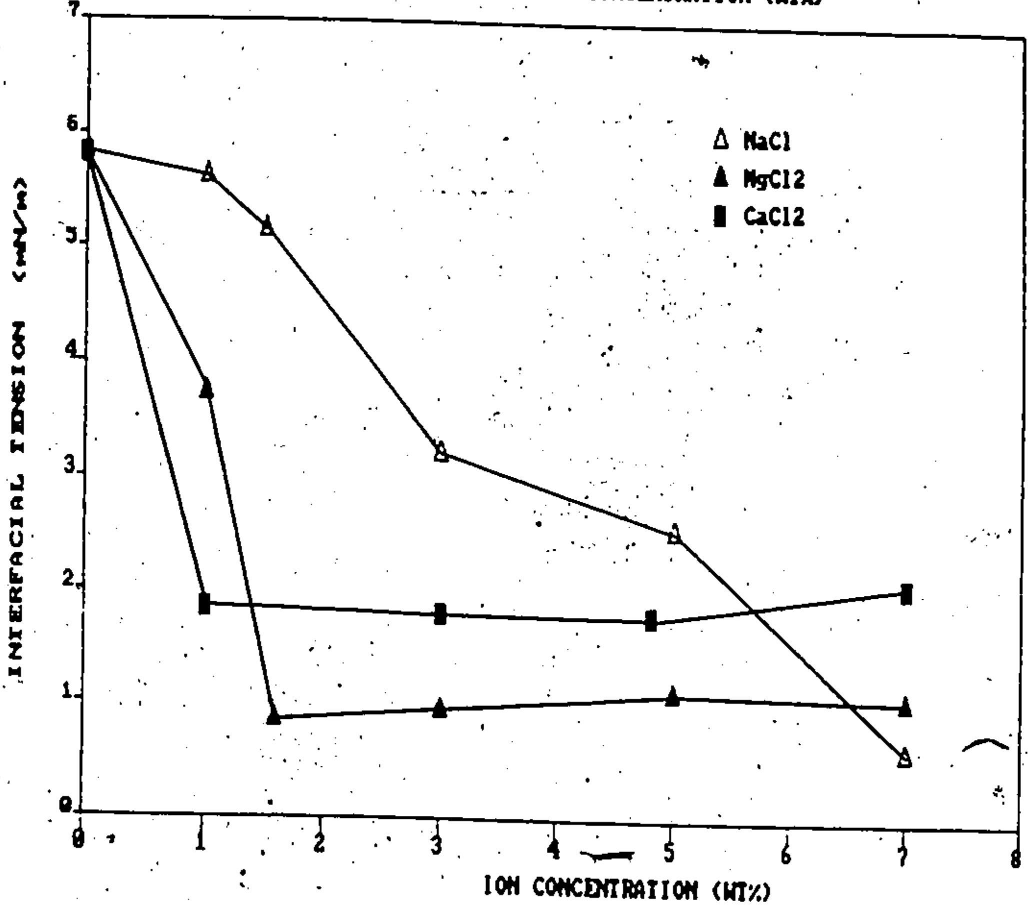
The interfacial tensions between the oil phase and various connate water formulations used in this study were measured both with and without surfactants present. The method has already been described in Section 4.1.

The results appear in Figures 25-26. In the case where there is no surfactant present (Fig.25), the interfacial tension between the oil and the connate water containing NaCl was the highest (up to a concentration of 5.5% NaCl). The next highest was the IFT between the oil and the connate water containing $CaCl_2$. The IFT between the oil and solutions of $MgCl_2$ had the lowest values, at least over a wide range.

The connate water formulations used in the present study were :

1.5% NaCl by weight
4.8% $CaCl_2$ by weight
1.6% $MgCl_2$ by weight

Fig.25- INTERFACIAL TENSION vs. ION CONCENTRATION (WT%)



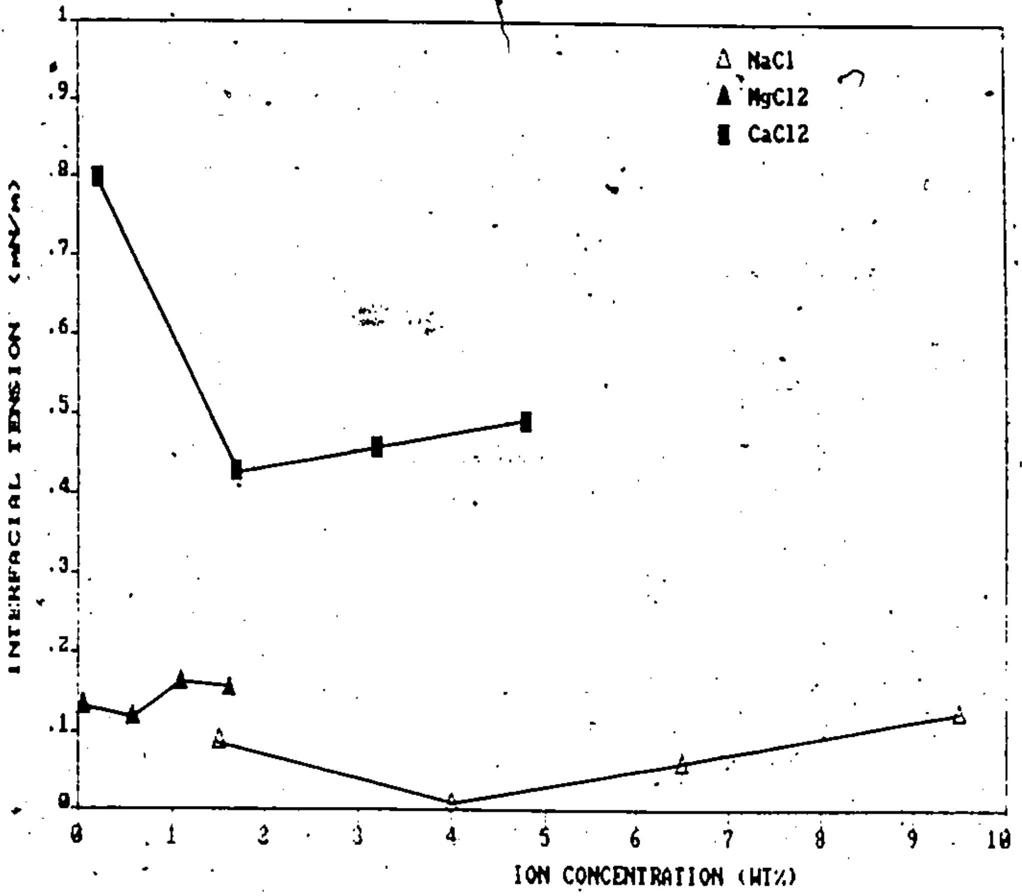
For these formulations, the solutions having the decreasing values of IFT are in the order of NaCl, $CaCl_2$ and $MgCl_2$.

Next, interfacial tensions were measured in the presence of a 0.2% (wt) solution of the surfactant Petrostep-420 and 1.5% NaCl. The results appear in Fig.(26). Obviously the order of magnitude has changed. In other words, the IFTs between the oil and connate waters containing $CaCl_2$ have the highest values followed by the water containing $MgCl_2$, and lastly that of the connate water containing NaCl. Comparison of the two graphs indicates an approximate ten-fold (and in some cases more) reduction of IFT values upon the addition of surfactant.

Solution	IFT (mN/m)	
	With surfactant	Without surfactant
1.5% NaCl	0.086	5.13
1.5% NaCl, 4.8% $CaCl_2$, 1.6% $MgCl_2$	0.355	4.22

It is important to note that even though there is a difference between the values of the IFT between the oil and the connate waters containing different ions, this difference for the concentrations used in our study is never more than a factor of five. Another important consideration is that IFT can vary greatly with time. Therefore, these measurements were taken at an equilibrium state, which in some cases took about

Fig. 26- IFT vs. ION CONC. (WT%), SURFACTANT : 0.2% P-420



a day to attain. However, in our displacement tests, as we will see in Chapter 9, our experiments had to be done in exactly the same fashion.

The differences between the nature of the IFT measurement method using the spinning drop tensiometer (Section 4.1) and that in the real situation where the oil and connate water are in contact at very complex conditions (and not necessarily at equilibrium), prevent us from drawing meaningful conclusions with high degrees of certainty. As will be seen later, the results of IFT measurements match and support the oil recovery findings, but because of the above reasons we have been very cautious in relating these results directly and solely to the IFT measurements.

The study of the IFTs between the oil and binary connate water solutions containing NaCl, $MgCl_2$ and $CaCl_2$ in the absence of the surfactants has produced the results of Table (6).

Table (6)- IFTs of binary solutions

Solution	IFT (mN/m)
3.5% NaCl + 3.5% $MgCl_2$	1.17
3.5% NaCl + 3.5% $CaCl_2$	2.35
3.5% $MgCl_2$ + 3.5% $CaCl_2$	1.93

And a ternary 7% solution containing 2.33% of each salt

2.33% ($NaCl$, $CaCl_2$, $MgCl_2$)	1.68

Obviously the IFT values are very close, but it is felt that in the absence of surfactants, $MgCl_2$ contributes to the lowering of IFT. Next we chose an ionic strength of 0.75 for each of the chloride solutions and calculated the corresponding concentrations. The solutions were prepared and IFTs against the oil were measured. The results are shown in Table 7.

Table (7) IFTs for the solutions of equal ionic strength (=0.75)

Solution	IFT (mN/m)
4.383% $NaCl$	2.70
2.775% $CaCl_2$	1.90
2.380% $MgCl_2$	0.88

Again the IFT for the case where Mg ions are present has the lowest value of all. Nevertheless, the difference between these IFTs is not considerable in terms of practical EOR schemes.

6.2-Contact Angle Study

At this stage of the research, we encountered a great deal of difficulty in measuring the water-oil-solid contact angles. The main reason for this was the partial miscibility and mixing of the oil and water due to the low viscosity and possibly high polarity of the Chatham crude oil. However, we performed some oil-water-air contact angle measurements on glass slides covered with a very thin layer of connate water and a drop of oil on top of that. The values found for the two connate water formulations used in this study were as follows :

Table (8)-Contact angle measurement results

Solution	$\theta_{min.}$	$\theta_{max.}$
1.5% NaCl	6.1	6.5
1.5%NaCl 4.8% $CaCl_2$ 1.6% $MgCl_2$	9.1	10.0

It was found that the values of contact angle decrease exponentially with time.

In a water-wet porous medium, oil is in the form of blobs and ganglia occupying mainly the large pores. However, if the porous medium is an oil-wet one, the oil would occupy small capillaries and would also cover the surface of the solid particles as a thin film. As we will see later, our observations suggested that the existence of the divalent ions would make the porous medium more water-wet. In other words, when divalent ions are present the oil would primarily be in the form of ganglia and blobs and would not spread and attach to the surface of the glass particles as strongly as in the case when there were no divalent ions present. This by itself (not considering other factors), might suggest a better recovery of oil when divalent ions are present in the connate water.

CHAPTER VII

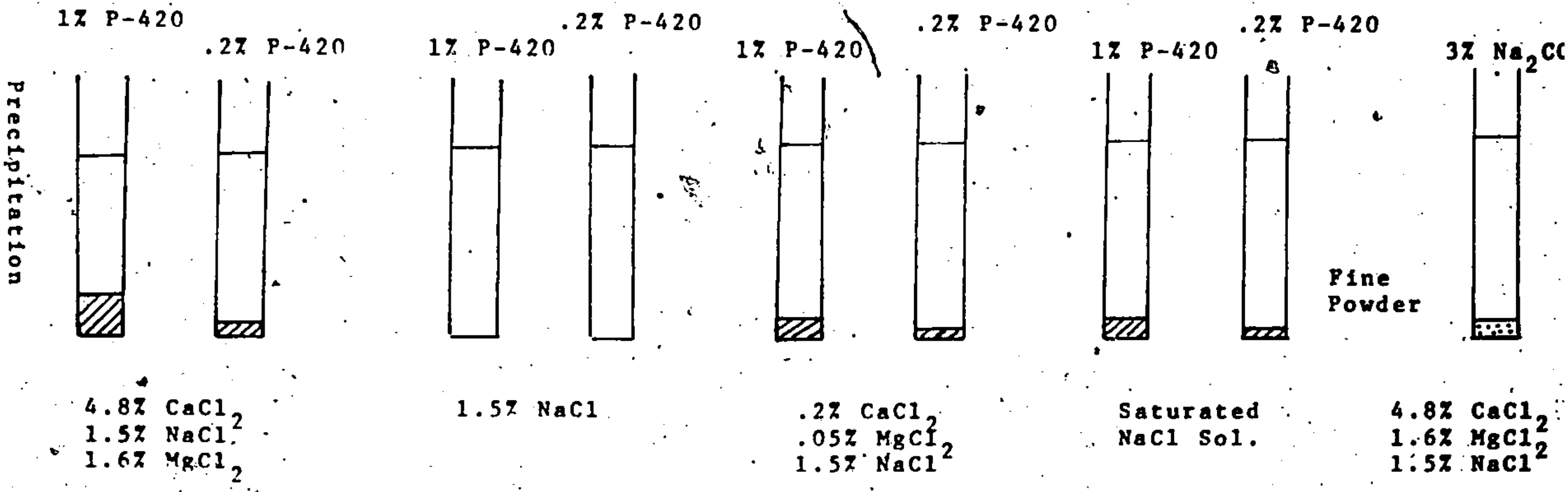
PRECIPITATE FORMATION AND PORE BLOCKAGE PHENOMENON

7.1-Precipitate Formation

In order to investigate the phase behavior of the connate water and the surfactant solutions during their contact, some simple experiments were designed and carried out in test tubes. These experiments involved solutions of dilute (0.2%) and more concentrated (1%) Petrostep-420 surfactant as well as solutions containing various amounts of electrolytes that we were interested in. Each time the two solutions were placed in contact with each other in the same manner. A summary of the results is depicted in Fig. (27) and can be explained as follows : Inorganic ions will cause precipitation of the sulfonates when concentration of either the salt or the surfactant is increased. In the case of NaCl this occurs at a rather high concentration, while addition of a small amount of divalent ions to even dilute solutions of surfactant will result in formation of precipitate.

The important point observed in our experiments was that an electrolyte solution containing only 1.5% NaCl would not form precipitate with P-420, even at high surfactant

Fig. 27 - Phase Behaviour Tests



concentrations of 4-5% (wt). However, the other connate water formulation used in our displacement tests, namely the one containing 1.5% NaCl, 4.8% $CaCl_2$ and 1.6% $MgCl_2$, formed large amounts of a sticky dark brown precipitate which was separated from the solution by centrifuging the solution. Microscopic examination of this very high viscosity material revealed the absence of any solid particles. This substance changed its appearance quite significantly with time. More precisely, after a period of a few hours it turned into a black sticky glue-like material, very similar to P-420 itself. This precipitate was also found to be quite capable of sticking to the glass beads and blocking some of the pores of the porous medium. This was observed both in simple tests involving glass beads and the precipitate, and in the core holder at the end of the tertiary recovery process, as we will see later in this chapter.

Celik et al (40) found that multivalent ions undergo complex behavior involving precipitation followed by redissolution of the precipitates at higher surfactant concentrations. This kind of redissolution is determined by the formation of the micelles that can solubilize the precipitated sulfonate. Addition of NaCl to a solution containing calcium sulfonate precipitate can also redissolve the latter. However, further addition of NaCl will cause reprecipitation of the surfactant.

This is the reason why in our experiments we used a solution of divalent ions and some NaCl as a salinity control to reduce excessive sulfonate precipitation by divalent ions.

7.2-Pore Blockage Phenomenon

The above observations compelled us to look for a mechanism which could explain what actually happened in the porous medium when the precipitate was formed. We are proposing the following mechanism which seems quite reasonable and logical. In the regions and pores where connate water containing divalent ions is the major occupant (middle pore, Fig. 28), the contact of the surfactant and divalent ions would form a precipitate which in effect would partially or completely block those pores. Then the surfactant flood would have to find pores and passages that had not been already blocked, namely those pores occupied by oil. This would increase the sweep efficiency and would result in a higher oil recovery. However, when the surfactant concentration increases, redissolution of the precipitate could occur which in turn would reduce the oil recovery. The results of our oil displacement tests (Chapter 9) confirm these assertions.

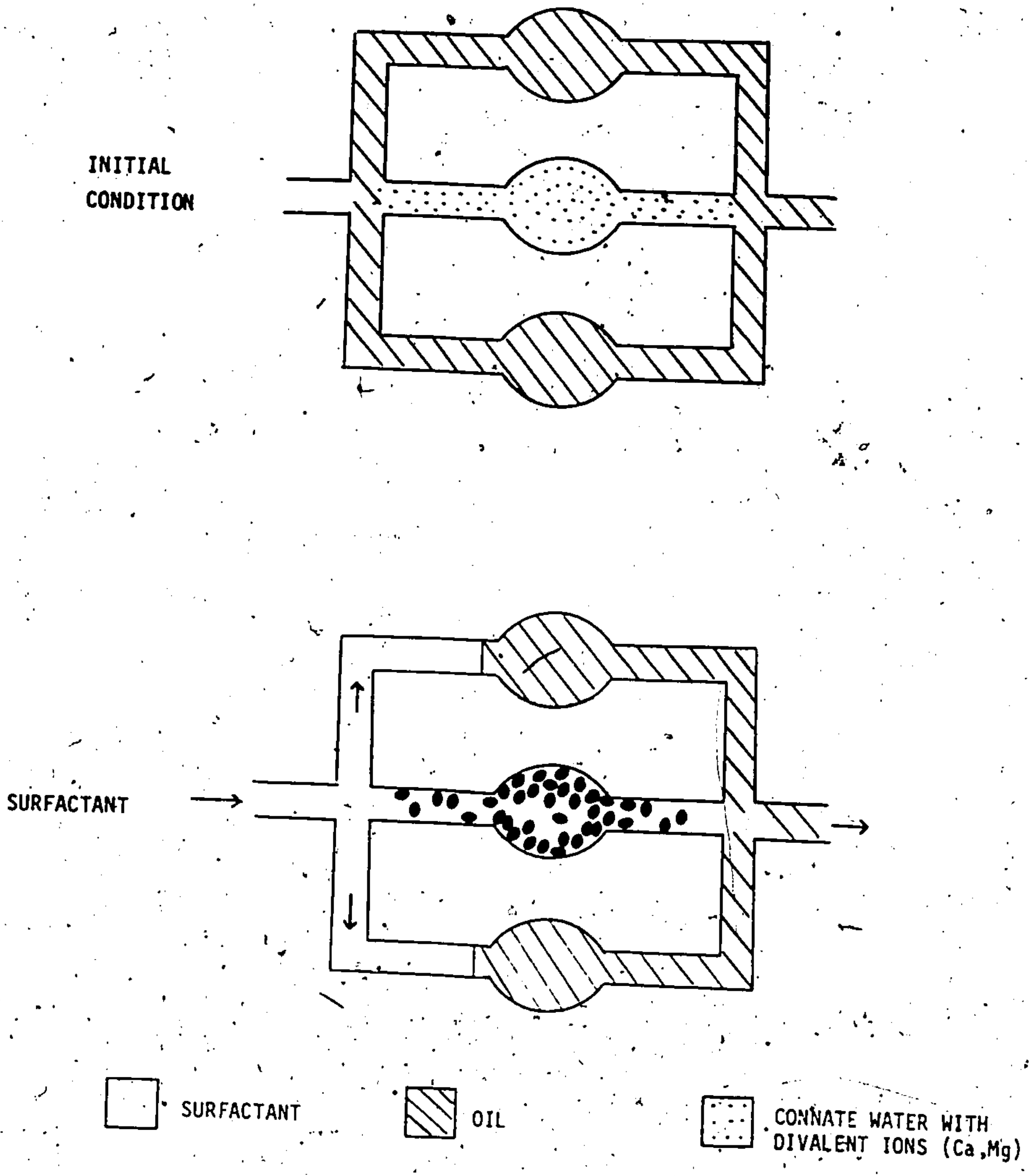


Fig.28-PORE BLOCKAGE MECHANISM

CHAPTER VIII

GANGLIA FORMATION AND FINGERING PATTERNS

8.1-Ganglia Formation

A ganglion is a nodular blob of a non-wetting phase that occupies at least one and usually several adjoining chambers of the void space in a permeable medium (44). After the primary and secondary recoveries, on the average two thirds of the OOIP remains trapped in the reservoir. This residual oil exists in the form of discrete oil ganglia and occupies 25 to 50% of the porous space. The other 50 to 75% is occupied by the aqueous phase which in our case is the connate water.

The ganglia are usually produced through shedding of blobs by the retreating oleic phase during secondary flooding. This takes place when fingerlike protrusion of the oleic mass forms a narrow neck under the combined effect of local pressure difference across the interface, ΔP_{neck}, and the interfacial tension, γ_{ow} (Fig. 29). If ΔP_{neck} is sufficiently large, the interface at the neck becomes unstable and the neck ruptures. In 1980 Mohanty, Davis and Scriven (45) predicted that neck rupture occurs if the following criterion is satisfied :

$$\Delta P_{neck} > 4\gamma_{wo}/d_p \qquad (12)$$

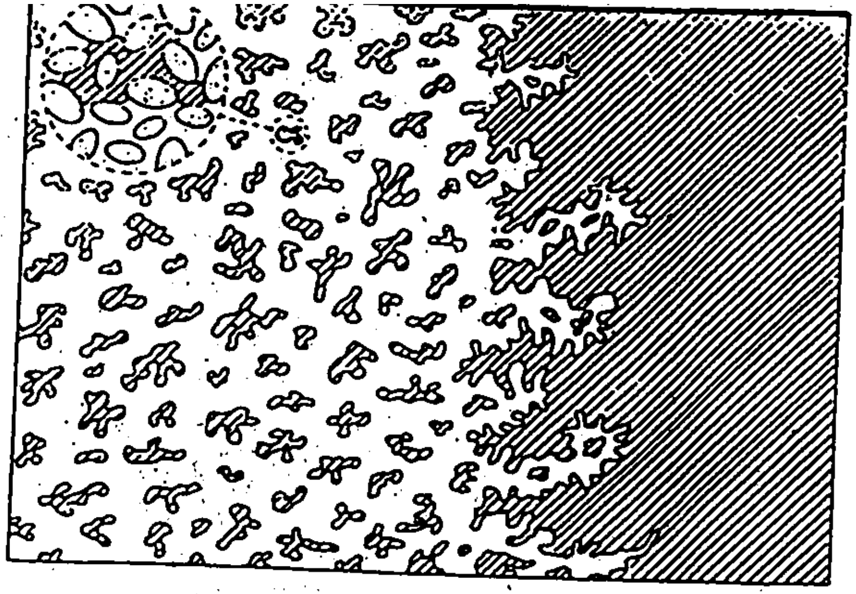


Figure 29 Schematic representation of immiscible oil displacement and formation of oil ganglia by waterflooding: hatched areas = oil, clear area = water, dotted areas = solid. The grains are only shown in the detail (inset). (44)

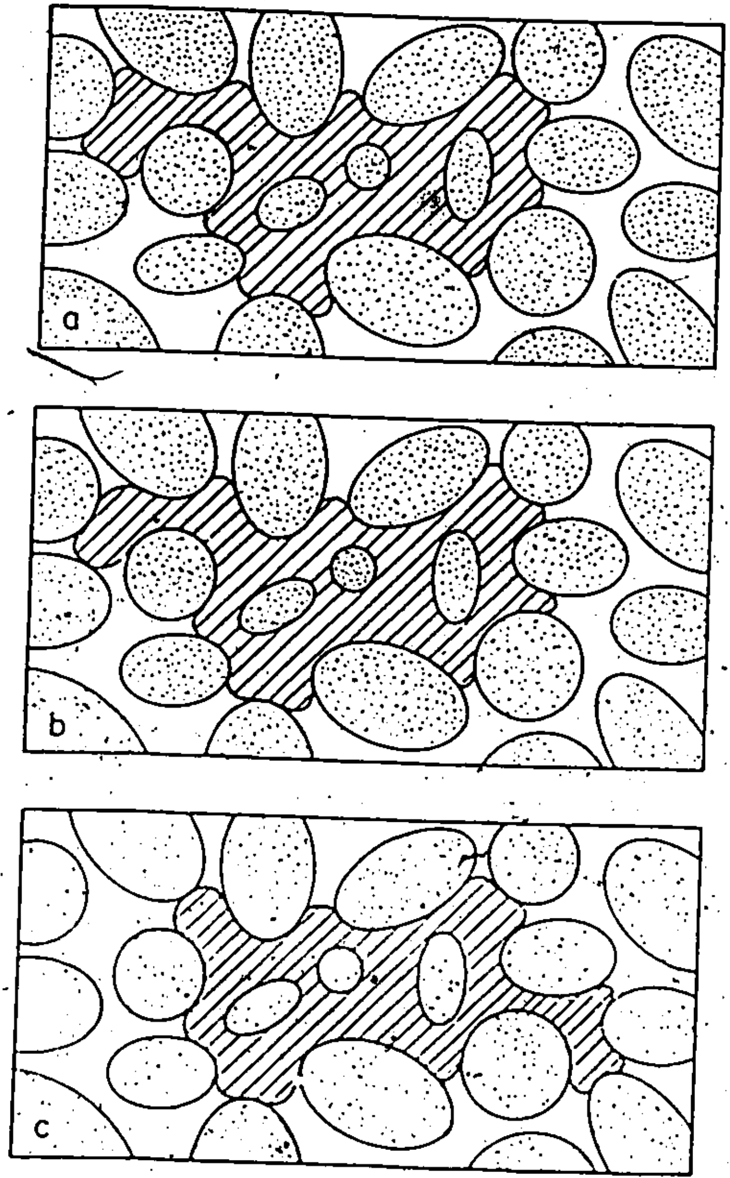


Figure 30 Mobilization of an oil ganglion. (*a*) No flow, ganglion at equilibrium (*b*) The aqueous phase flows from left to right with pressure gradient less than the critical value required for mobilization. (*c*) If the pressure gradient where d_p is the volumetric diameter of the pore chamber adjacent to the neck. The oil ganglia formed in this manner do not usually travel far. The distance over which a given ganglion travels before it gets stranded is a function of the ganglion size, the contact angle, the porous medium geometry, the water saturation (S_w) and the capillary number.

During the oil displacement tests in this study, it was noticed that depending on the composition of the connate water in place, there were different fingering and ganglia formation patterns. These phenomena were consistently observed during all of the experiments. To be more explicit, when the connate water contained NaCl only, the fingers were very small and short and the aqueous front (displacing phase) moved quite regularly and uniformly in such a way that the swept area left behind did not contain any major large-size oil banks or ganglia. The whole area seemed to have been swept uniformly.

On the other hand, when divalent ions were present in the connate water (1.5% NaCl, 4.8% $CaCl_2$ and 1.6% $MgCl_2$), the displacement pattern looked very different. First of all, there were many unswept areas left behind and it seemed that the displacing phase was bypassing many areas of the reservoir. Another important aspect was the wide and long shape of the fingers. The swept area looked like a "leopard skin" containing many small dark patches that were oil ganglia and oil banks trapped in the pore spaces. As the experiments advanced, more and more of these oil ganglia were pushed towards the, outlet and the medium became brighter. The injection of surfactant in tertiary recovery swept these areas and a dark front could be seen moving and washing these dark oil ganglia regions.

Since the permeability of the porous medium was higher at the regions adjacent to the plexiglass core holder wall, an effort was made to make sure that this phenomenon was not occurring only at the neighborhood of the wall. The close examination of the interior core confirmed that this process occurred in all regions of the porous medium. Numerous photographs were taken during each process. The schematic drawings in Fig. (31) represent some of these patterns.

At the next stage we decided to find out which factors were responsible for this strange behavior. Since the only difference between the experiments was the existence of divalent cations, displacement tests were conducted with connate waters containing only one of the electrolytes at a time. The results showed that it was the magnesium and, to a lesser extent, calcium ions which were responsible for this ganglia formation and irregular fingering phenomenon. In trying to find out more about the mechanism of this process, IFT, pressure drop and viscosity measurements were conducted

Fig. 31 - Fingering Patterns

in detail. As depicted in Fig. (25), the decreasing order of magnitude of the IFT for connate water solutions each containing one of our three electrolytes corresponds to NaCl, $CaCl_2$ and $MgCl_2$ i.e.,

$$\gamma_{owMg} < \gamma_{owCa} < \gamma_{owNa}$$

In addition, the viscosity of the ternary connate water solution containing 1.5% NaCl, 4.8% $CaCl_2$ and 1.6% $MgCl_2$ was about 20% higher than the one containing 1.5% NaCl alone. However, in tests involving connate water solutions with equal ionic strengths (4.38% NaCl - 2.77% $CaCl_2$ - 2.38% $MgCl_2$), even though the viscosity of the NaCl solution was about 5% higher than that of the other two solutions, the previously mentioned strange pattern and fingering behavior was only observed with solutions containing divalent ions and not with NaCl solution. This suggested that although the viscosity can change the pressure drop across the neck of the finger and therefore influence the ganglia formation, the rather small 20% viscosity difference in our case could not be the detrimental factor (higher viscosity of the connate water solutions containing divalent ions can increase the sweep efficiency and thereby the oil recovery).

Looking at this phenomenon from an IFT point of view, we find that the ratio between the IFT values in some cases is as high as 300% (e.g., $MgCl_2$ and NaCl solutions). With this observation and assuming a constant d'_p in our ganglia formation criterion, it could easily be concluded that there is much more possibility of finger neck rupture and therefore ganglia formation when the connate water consists of divalent cations than when it contains sodium cations alone. Nevertheless, we believe that in this very complex process there are other factors which must be taken into consideration such as the wettability and electrochemical properties of each of the individual ions, as well as oil electrolyte interactions. These areas were, however, beyond the scope of this research project.

CHAPTER IX

OIL DISPLACEMENT TESTS

As mentioned earlier, the displacement tests were conducted using two strategies. Strategy I was initiated with waterflooding (secondary recovery) which took about ten hours to prepare and complete. The tertiary recovery was commenced the following day. First experiments with the core holder in a horizontal position showed that the gravitational force could play a role during the time interval between the secondary and tertiary recoveries. More precisely, since there is a difference between the density of oil and various connate water solutions, the residual oil (unrecovered oil at the end of secondary recovery) would travel to the upper half of the porous medium. Although this mobile oil was recovered during tertiary recovery, it was decided to do some of the tests in a vertical mode, where the gravitational force would slightly assist the recovery.

There was no clear phase separation or oil mobilization in the case of vertical displacements, possibly because the trapped oil in the larger pores (the oil that could be mobilized by gravity during the waiting period between secondary and tertiary recoveries) had already been mobilized and recovered during the secondary recovery. Another possibility could be that in the case of horizontal flooding, the gravity would push the oil upward towards the more permeable areas around the cell walls, whereas in the vertical case the force of gravity was only effective along the length of the cell towards the outlet which is a path along which the relative permeability to water constantly decreases (amount of unrecovered oil increases towards the outlet of the cell).

Most of the displacement tests were performed twice and the results shown here are the average values. In general, the reproducibility of the experiments was satisfactory. The relative error was never more than 1-2%. The results of the Strategy II experiments are now described.

Two experiments were designed to investigate the effects of surfactant aging. The conditions were identical except that in one of the experiments (run 6) a three week old surfactant was injected into a porous medium which was 88% saturated with oil (12% connate water containing 1.5% NaCl), while the other cell was flooded with fresh surfactant solution. Both surfactant solutions were made of 0.2% Petrostep-420 and 1.5% NaCl. As seen in Fig.(32), from the early stages of the recovery (after 1.5 PV), more oil has been recovered with fresh surfactant

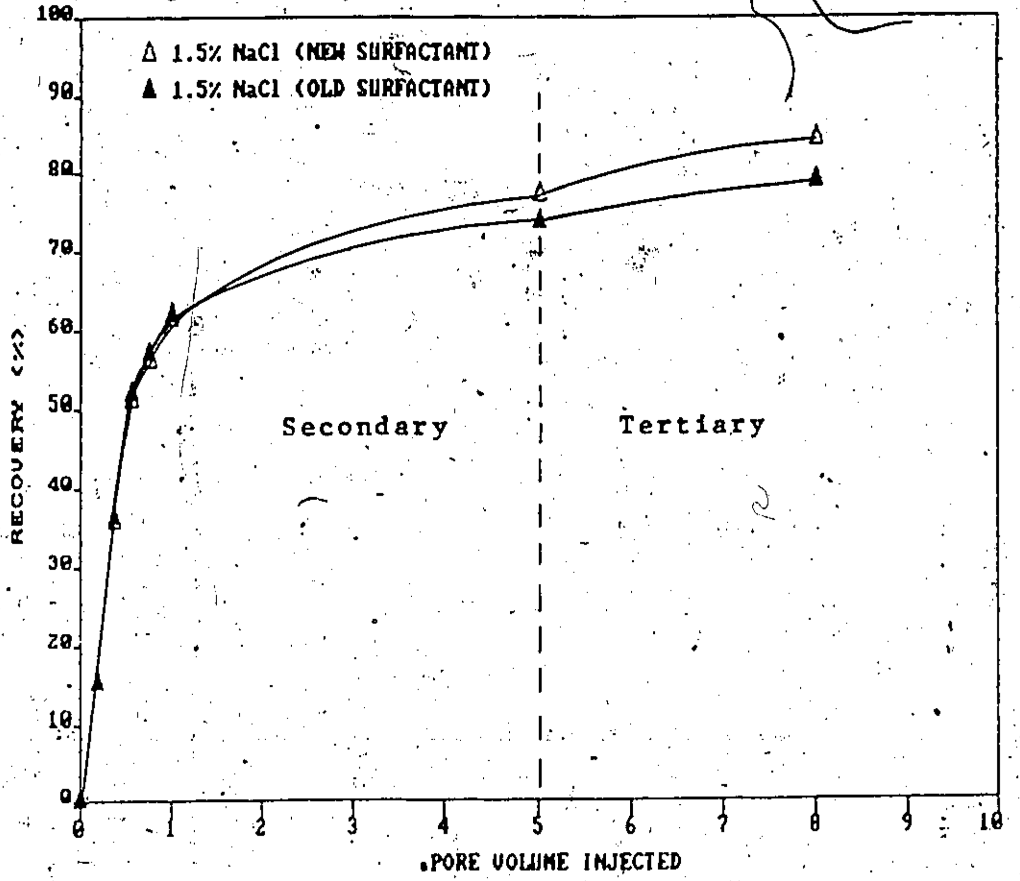
STRATEGY		
	SECONDARY	----------
	TERTIARY	5-8 PV SURFT.

H 7

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (5 P.V.)				TERTIARY REC. (8 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	5 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	8 PV (%)
1	1.5% NaCl NEW SURFT.	35.58	1.72	88.26	.256	.086	.692	61.10	77.10	.086	.692	84.13
6	1.5% NaCl OLD SURFT.	35.74	1.81	88.14	.256	.086 ?	.692 ?	61.86	73.66	.086 ?	.692 ?	78.76

Fig. 32 - PRODUCTION HISTORY RUN NO.: 1,6



than with the old one. This difference was about 3.5% at 5 PV and 5.5% after 8 PV of surfactant flooding. The reason lies in the fact that the old surfactant had lost some of its IFT lowering properties and therefore could not recover oil as efficiently as the fresh surfactant solution. It was then decided to use fresh surfactant solutions for all future runs.

Runs 1 and 2 (Fig. 33) were carried out using connate water solutions containing different electrolyte compositions. One with 1.5% NaCl only and the other containing a high concentration of divalent ions (4.8% $CaCl_2$, 1.6% $MgCl_2$) as well as 1.5% NaCl. The ionic strength of the second solution was about 8 times higher than the one containing 1.5% NaCl. Although the capillary number for the first solution is greater than that of the second one, we can see from the production history curve that, up to 5 PV of surfactant flooding, the oil recovery for the cores containing divalent ions was higher than that with no divalent ions (4% higher at 5 PV). Based on our observations we believe this is caused by the pore blockage effect due to precipitate formation described in Chapter 7. However, towards the end of the experiments, the dynamic and viscous forces caused by the new surfactant flood were pushing most of the precipitate out of the pores and towards the outlet.

Furthermore, since the amount of the connate water and the concentration of the divalent ions were decreasing with time

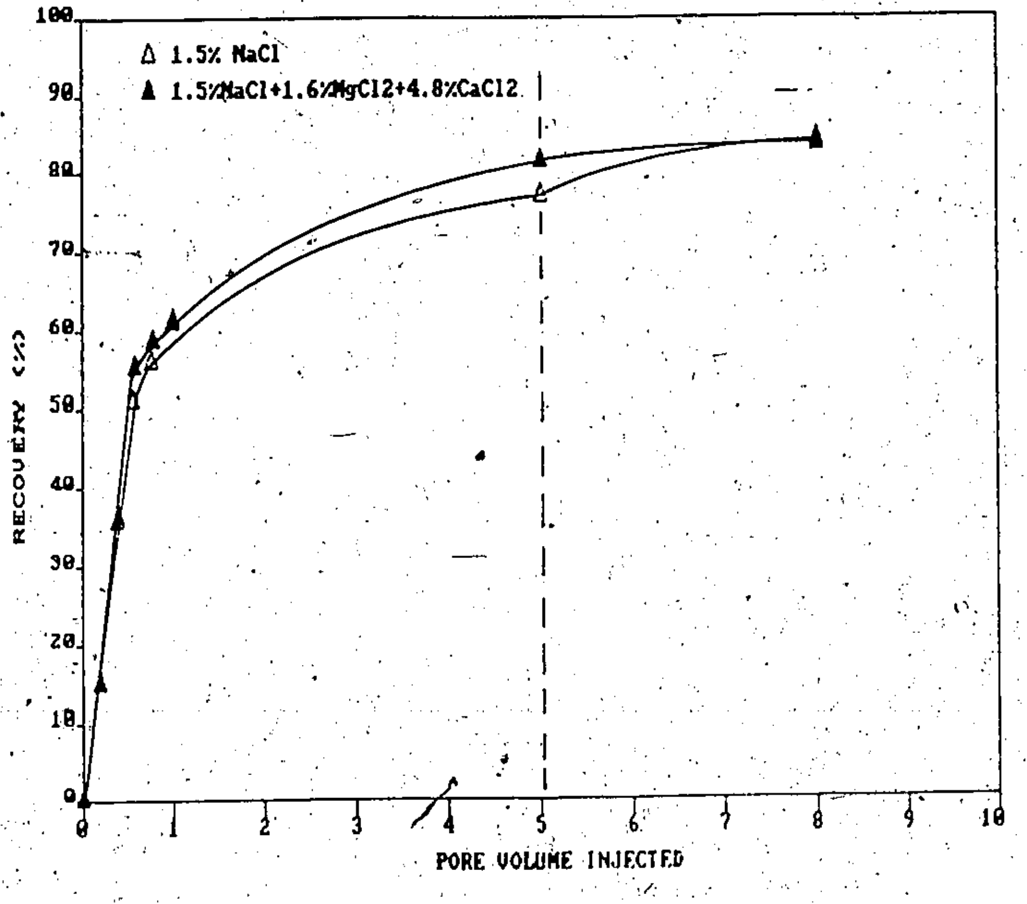
STRATEGY		
	SECONDARY	------------
	TERTIARY	5-8 PV SURFT.

H

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	Ø (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (5 P.V.)				TERTIARY REC. (8 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	5 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	8 PV (%)
1	1.5% NaCl	35.58	1.72	88.26	.256	.086	.069	61.10	77.10	.086	.692	84.13
2	4.8% $CaCl_2$ 1.5% NaCl 1.6% $MgCl_2$	34.74	1.78	88.43	2.058	.355	.166	60.82	81.43	.355	.166	83.39

Fig. 33 - PRODUCTION HISTORY RUN NO.: 1,2



(dilution effect caused by the surfactant flood), there must have been less and less precipitation formation. This explains why the slope of the production curve for the case where divalent ions were present decreases towards the end of the recovery process. On the other hand, due to lower IFT, the amount of oil recovered from the porous medium containing NaCl only is constantly increased without dramatic complications.

After 1-2 PV of surfactant flooding most of the connate water originally in place (about 10% of PV) is replaced by surfactants. Consequently, it becomes very difficult to investigate any possible effects of connate water composition on the recovery process. Therefore, it was decided to perform future tests using Strategy I, namely secondary connate water flooding to remove most of the OOIP and the tertiary recovery to produce the remaining residual oil. In this fashion, by the end of the secondary recovery, nearly 60-70% of the pore volume has been occupied by brine containing electrolytes in which we are interested. Then any possible effects of those ions will be more obvious.

Sometimes in the field it is customary to omit the secondary water flood completely and go directly to tertiary surfactant flooding. In this case the electrolyte concentrations at the beginning of the flood might still be high but obviously the quantity of connate water present would be very small.

Therefore, the amount of the precipitate formed may not be large enough to produce any observable pore blockage effect such as that seen during Strategy 1.

With regard to these facts the decision was made to perform the future displacement tests using Strategy I, i.e. 5-6 PV waterflooding followed by 3-4 pore volumes of surfactant (tertiary) injection.

The results of a typical displacement test using Strategy I are shown in Fig. (34). After only 1 PV of waterflooding about 60% of the OOIP is recovered (large slope of the production history curve). The reason lies in the fact that since in the beginning the reservoir is almost 90% saturated with oil, the dynamic and viscous forces of the water flood are sufficient to drive most of the oil occupying the large pores out of the porous medium. But then the rate of recovery slows down and at 6 PV of waterflooding there is virtually no more oil recovered (production curve becomes almost horizontal). At this stage most of the 26% remaining (residual) oil is trapped in very small pores which the water flood alone is not able to recover. Up to this time, the recovery process has involved physical forces alone but to recover extra oil we would need to use a chemical process as well. This is when we start our

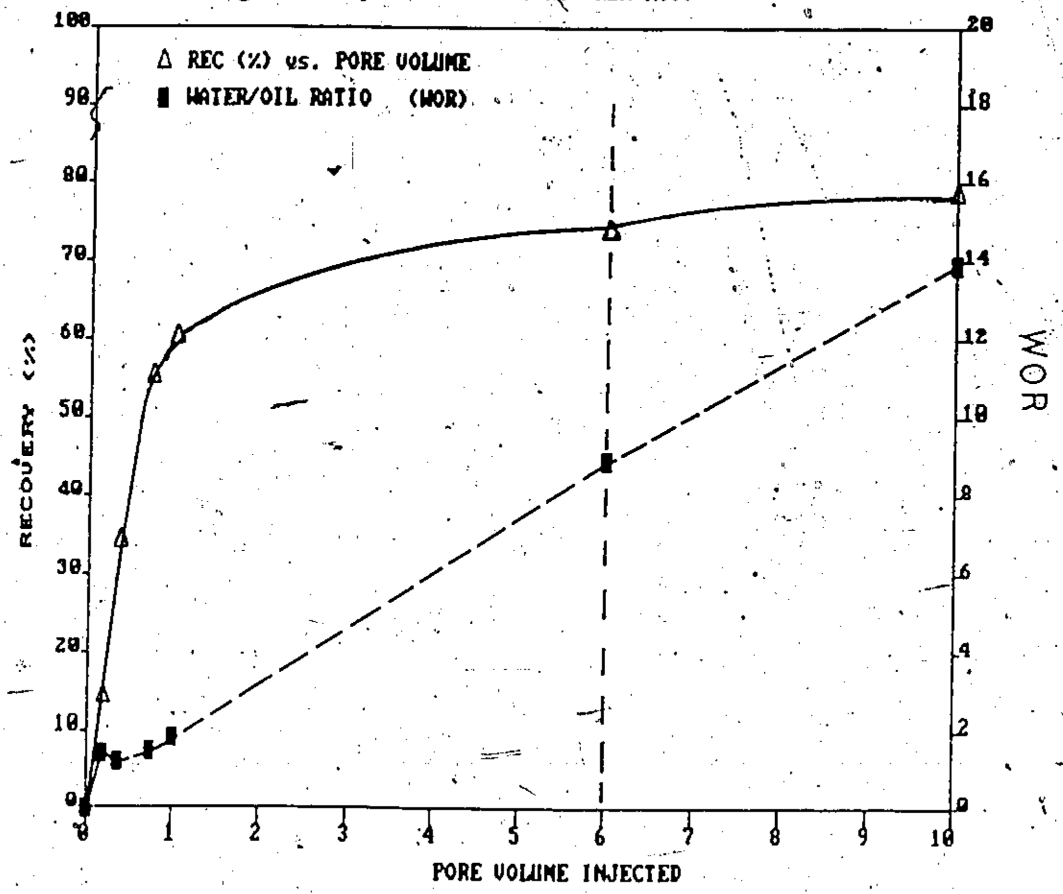
STRATEGY		
	SECONDARY	6 PV PURE WATER
	TERTIARY	4 PV SURFT.

V

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (6 P.V.)				TERTIARY REC. (10 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	6 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	10 PV (%)
26	PURE WATER	34.84	1.94	91.22	0	5.80	.010	59.87	73.71	----	----	78.52

Fig. 34-PRODUCTION HISTORY RUN NO.: 26



tertiary recovery using the surfactant solution of 0.2% (wt) P-420 and 1.5% NaCl. The surfactant's ability to reduce oil/water IFT makes it easier for the displacing flood to mobilize and recover the residual oil trapped in small pores. This part of the recovery is both a physical as well as chemical process.

On the lower part of Fig.(34) is the so-called water/oil ratio curve (WOR). It simply represents the ratio of the volume of the displacing phase (water and surfactant) to the volume of the displaced phase (oil). From the economics point of view, WOR is an important factor to be considered. In practice WOR values greater than 20 are not considered economical in EOR. The irregularity at the very beginning of the WOR curve is simply due to the fact that in this stage of the process the amount of oil recovered is almost equal to the quantity of the water injected (i.e. the breakthrough has not yet occurred). Naturally this cannot continue for long and soon the slope of the WOR curve stabilizes. This curve could have been plotted for each individual experiment. However, it is not of major interest, so for the sake of clarity of the production history curves the WOR has not been represented on all the graphs.

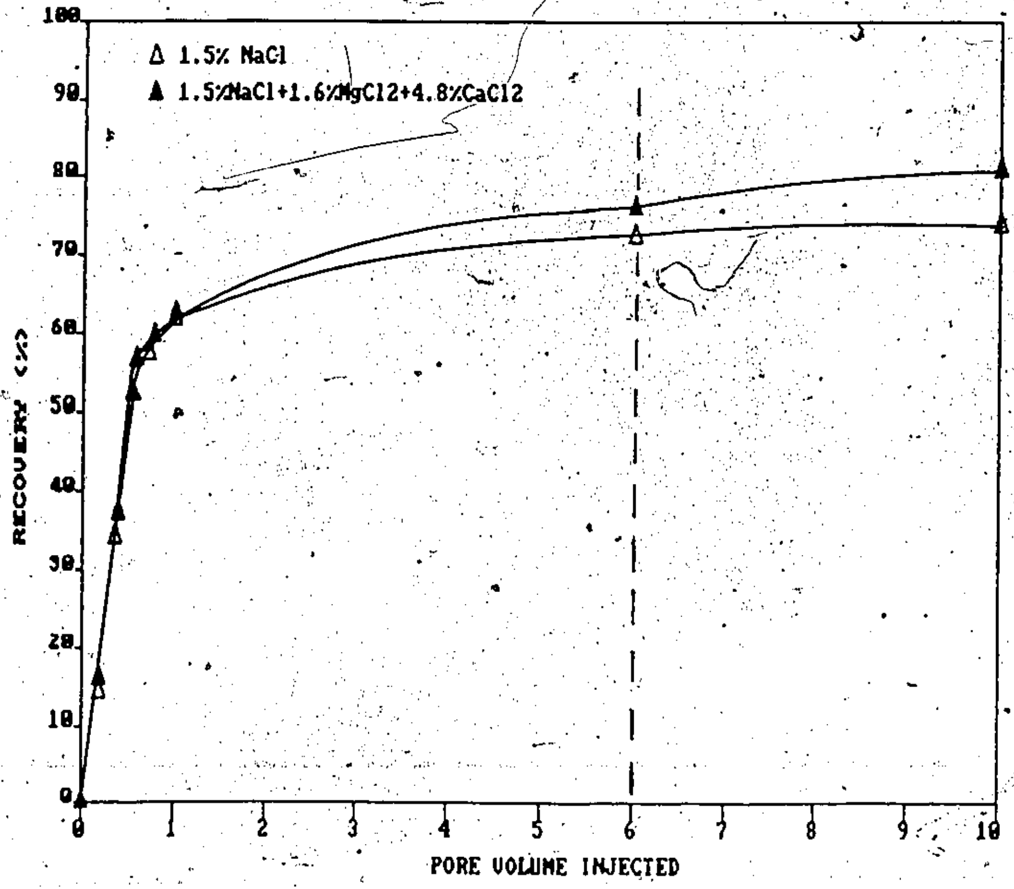
Experiments No. 17 and 18 (Fig. 35) are identical except for the fact that in run 18 divalent ions have been added to

STRATEGY	SECONDARY	6 PV C.W.
	TERTIARY	4 PV SURFT.

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (6 P.V.)				TERTIARY REC.(10 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	6 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	10 PV (%)
17	1.5% NaCl	35.64	1.87	86.96	.256	5.13	.012	61.51	72.49	.086	.719	73.72
18	1.5% NaCl 1.6% $MgCl_2$ 4.8% $CaCl_2$	34.98	1.83	89.72	2.058	4.22	.017	62.42	75.86	.355	.174	80.99

Fig. 35 - PRODUCTION HISTORY RUN NO.: 17,18



the connate water. After almost 1 PV of waterflooding, the production curve of run 18 starts to show higher values of recovery. At the end of the secondary recovery (6PV), this difference is more than 3%. As we have discussed earlier in sections 6.2 and 8.1, divalent ions may make the porous medium less oil-wet and this might be the reason behind higher recovery during run 18. In fact the ganglia observed in this case could have been formed due to this wettability related phenomenon. At the same time, the fact that the viscosity of the connate water used in run 18 was about 20% greater than the one used in run 17 should contribute somewhat to this increase in recovery through better sweep efficiency. This increase in oil recovery became even more obvious during the tertiary recovery, and at the end of the surfactant flooding it has reached a 7% value. We consider the pore blockage effect described in Section 7.2 responsible for this increased recovery during tertiary recovery.

The displacement test data of Fig. (35) show a capillary number of 0.174 for run 18 compared to 0.719 for run 17 (during tertiary recovery), at the same time the IFT of run 17 is lower than that of run 18 (0.086 and 0.355). Considering N_{ca} and IFT values alone, we would expect a higher recovery for run 17, i.e. when there are no divalent ions present. However, this is not the case and the fact that we encountered the same behavior again and again during subsequent experiments suggests that although N_{ca} and IFT are important factors, one cannot predict the performance of a reservoir and the oil recovery by N_{ca} and IFT data alone.

The ionic strength is the next item to be considered. The IS for run 18 is 2.058 compared to 0.256 for run 17. This, as we will discuss later, may play a role in determining the wettability behavior of the porous medium.

In trying to find out which of the two divalent ions could be responsible for a higher recovery, we performed experiments 19 and 20 (Fig. 36). At the end of the secondary flooding, the recovery for the systems containing $MgCl_2$ was the lowest of all which may be due to the fact that the very strange and irregular fingering patterns observed in this case have reduced the sweep efficiency resulting in poor recovery.

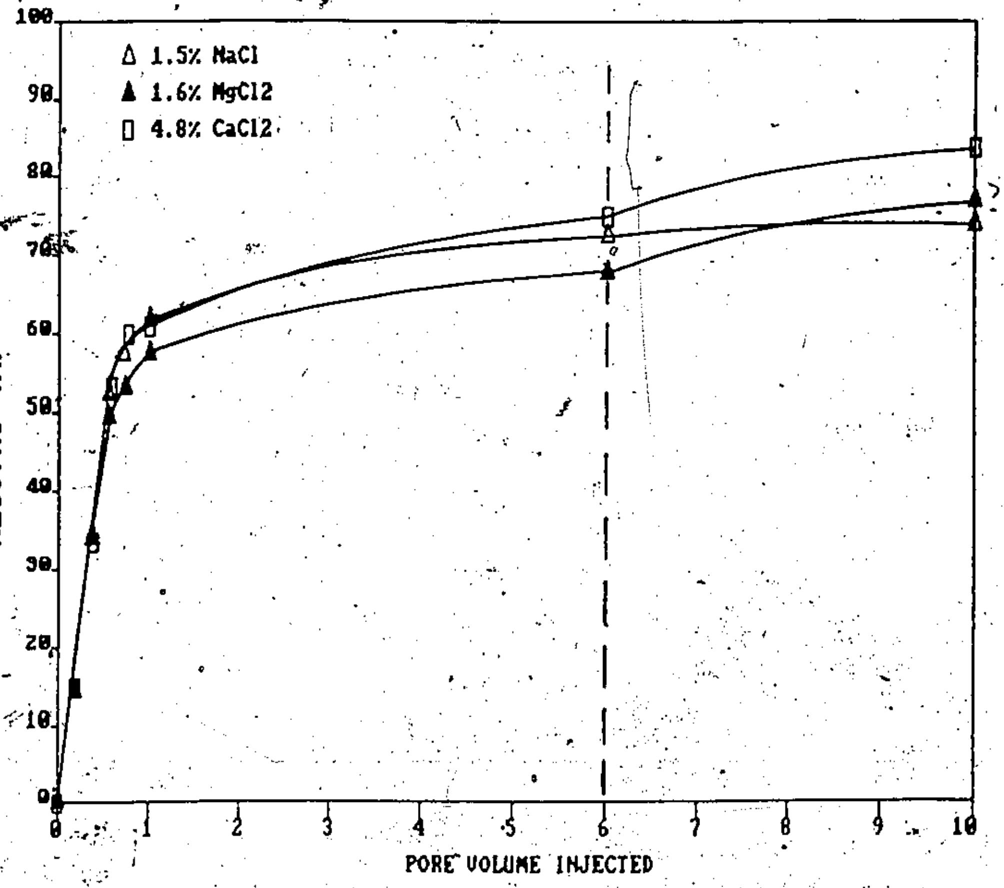
At the end of secondary recovery the pores contain about 60-70% connate water. The addition of surfactant to the porous medium containing NaCl alone does not produce much oil (less than 1%), while we observe sharp increases in recovery during runs 19 and 20 (about 9%). We believe that precipitation and the subsequent pore blockage mechanism are responsible for this behavior. On the other hand, the increasing order of recoveries observed is in the same increasing order of ionic strengths and IFTs and decreasing order of capillary numbers.

STRATEGY		
	SECONDARY	6 PV C.W.
	TERTIARY	4 PV SURFT.

V. DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (6 P.V.)				TERTIARY REC. (10 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	6 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	10 PV (%)
17	1.5% NaCl	35.64	1.78	86.96	.256	5.13	.012	61.51	72.49	.086	.719	73.72
19	1.6% $MgCl_2$	34.95	1.79	89.50	.504	.84	.073	57.15	67.54	.150	.408	76.71
20	4.8% $CaCl_2$	35.42	2.76	89.73	.298	1.81	.037	61.00	74.91	.450	.136	83.75

Fig. 36 - PRODUCTION HISTORY RUN NO.: 17,19,20



To increase our degree of certainty about the true nature of the oil recovery and the mechanisms involved, experiments 21 and 22 were performed (Fig. 37). Run 21 originally contained divalent ions but during secondary recovery it was flooded with a connate water containing NaCl only, in such a way that at the end of 6 PV secondary flooding most of the divalent ions present in the beginning of the experiment (about 10%) together with a large portion of the OOIP had been substituted by the connate water containing NaCl only (70-80% of the pore volume). The amount of the oil recovered in both secondary and tertiary recoveries are lower than those of run 22 which is the exact opposite case. It consisted of a porous medium originally containing NaCl alone and flooding it with 6 PV of a connate water containing divalent ions. Therefore, the subsequent surfactant flooding would result in precipitate formation and pore blockage which in effect would contribute to a higher recovery of about 5.5%.

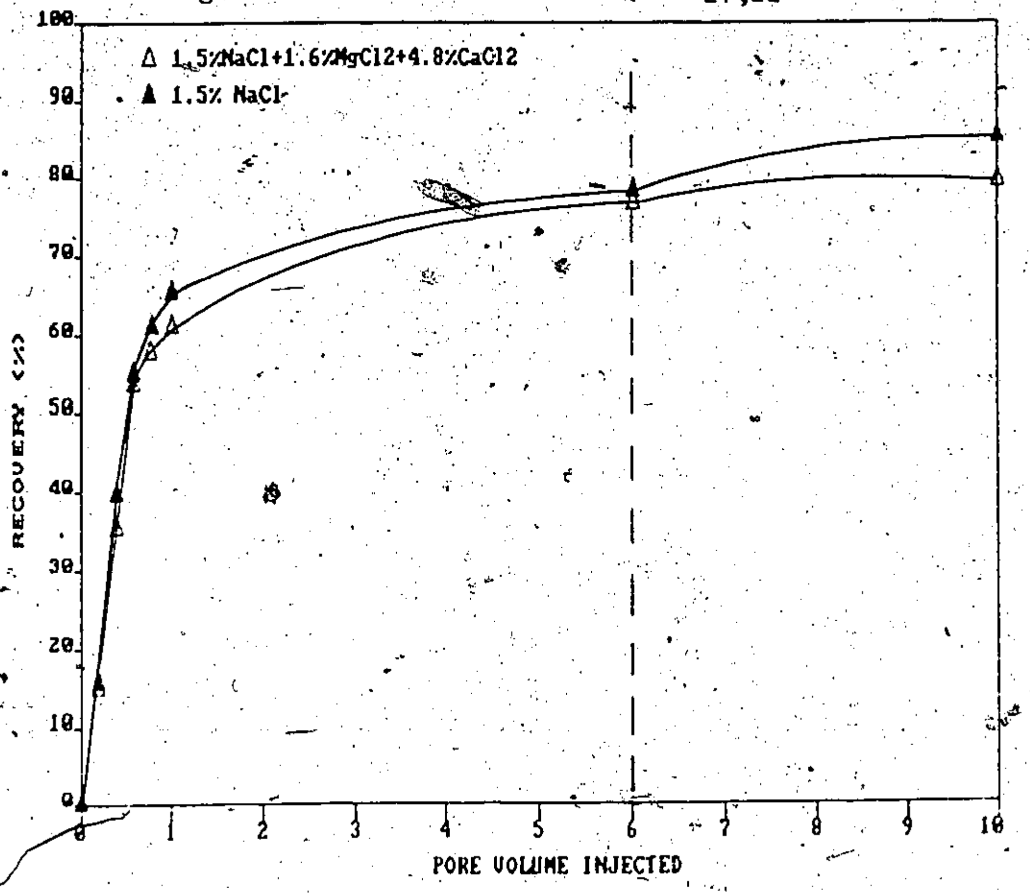
The next stage of the research involved experiments with systems having the same ionic strength of 0.75 (Fig. 38). At the end of the secondary flooding, the oil recovery for the case where calcium ions were present was slightly higher than the other two cases. Ganglia were formed in the case of $MgCl_2$ and, to a lesser extent, with $CaCl_2$. Then, during tertiary recovery, the rate of recovery increase is almost identical for all three cases (7-8%). The effect of IS on

STRATEGY		
	SECONDARY	6 PV OPP. C.W.
	TERTIARY	4 PV SURFT.

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (6 P.V.)				TERTIARY REC. (10P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	6 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	10 PV (%)
21	1.5% NaCl 1.6% $MgCl_2$ 4.8% $CaCl_2$	34.94	1.85	90.74	2.058 .256	4.22 5.13	.017 .012	60.84	76.68	.086	.719	79.53
22	1.5% NaCl	34.55	1.77	87.24	.256 2.058	5.13 4.22	.012 .017	65.33	78.33	.355	.174	85.00

Fig. 37 – PRODUCTION HISTORY RUN NO.: 21,22



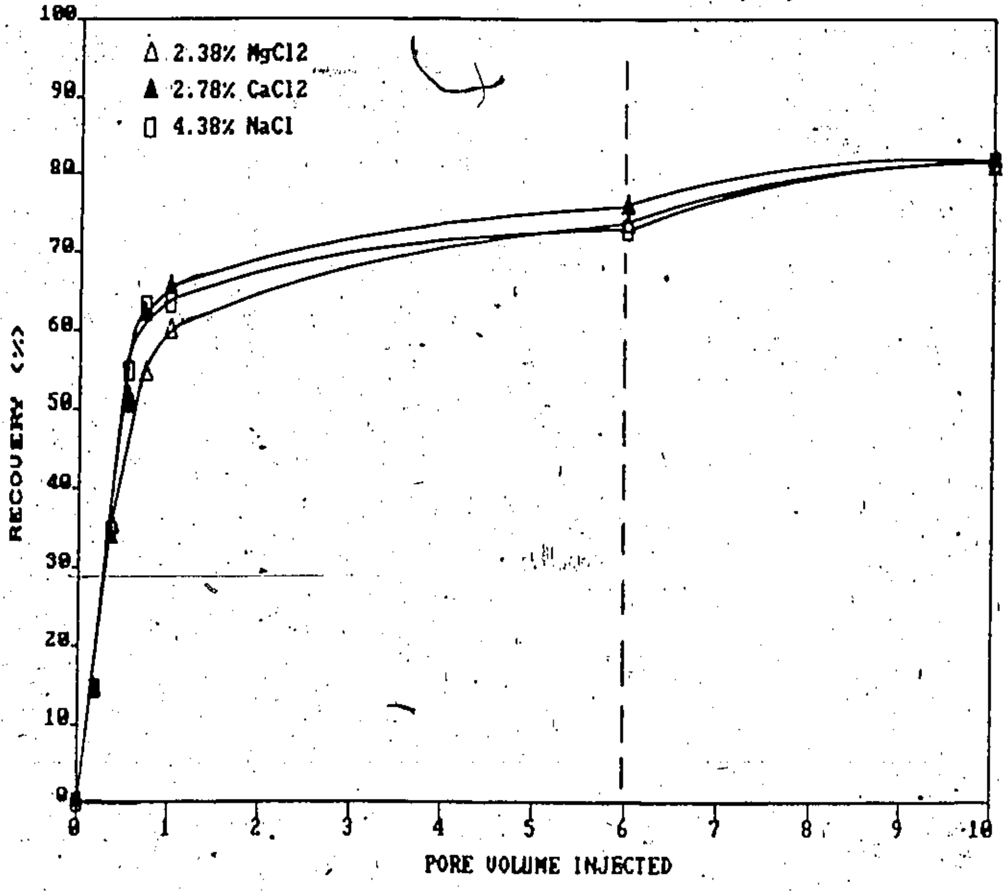
STRATEGY		
	SECONDARY	6 PV C.W.
	TERTIARY	4 PV SURFT.

V

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (6 P.V.)				TERTIARY REC. (10 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	6 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	10 PV (%)
23	2.38% $MgCl_2$	34.88	1.98	88.71	.750	.88	.069	59.64	73.24	.10	.613	80.66
24	2.78 $CaCl_2$	35.64	2.10	90.02	.750	1.90	.031	65.26	75.69	.60	.102	83.73
25	4.38% NaCl	35.14	1.83	87.92	.750	2.70	.023	63.55	73.02	.01	6.127	81.56

Fig. 38- PRODUCTION HISTORY RUN NO.: 23,24,25



recovery is believed to occur through its influence on wettability performance of the porous medium. Higher IFT and lower N_{ca} for the case of NaCl could explain the slightly lower recovery observed. The fact that the viscosity of 4.38% NaCl solution is about 10% greater than the other two solutions would reduce the mobility ratio

$$M = (K_w \mu_o) / (K_o \mu_w) \qquad (13)$$

and improve the recovery but obviously this increase in recovery through better sweep efficiency is not the dominant aspect in this case.

It should be noted that it is extremely difficult to predict and judge the performance of the displacement tests on the basis of individual factors involved, simply because during each stage of the experimental work there are various factors involved such as IFT, N_{ca}, IS, viscosity, contact angle and wettability properties of the system, S_{oi}, S_{or}, electrochemical effects, ganglia formation, pore blockage phenomenon and possibly many other known and unknown factors. They could well be dominant in one stage of the experiment and less effective in some others. While we are in most cases able to describe the individual effects of each factor, due to complexities of the system, it is impossible to describe the ensemble of the process with any high degree of certainty. In other words it is extremely difficult to point out any single factor as the dominant and detrimental aspect of the process. For instance, for a given experiment, high viscosity of the displacing phase and pore blockage effects could contribute to high oil recoveries, while at the same time high IFT and low capillary number would produce the opposite effect. At the same time there are many other contributing factors with different levels of contribution and while we can discuss them individually, it is very difficult to know exactly which one is the dominant one and what the outcome would be.

Margeson (35) has reported an almost constant IFT between Chatham oil and solutions containing 1.5% NaCl and 0.01-5% (wt) P-420 (Fig. 39). Therefore, in trying to cancel out any IFT effects, we performed some experiments with different concentrations of P-420 (within the range 0.01-3%). Since the degree of precipitation when surfactant comes in contact with divalent ions greatly depends upon the concentration of the surfactant, this would enable us to further investigate the nature of the pore blockage mechanism.

Experiments 11 and 12 (Fig. 40) involved solutions of 1.5% NaCl as the connate water. The porous medium was flooded with 5 PV of the same connate water until no more oil could be recovered. As we can see at this stage about 78% of the OOIP has been recovered. Next 3 PV of a Petrostep-420 and 1.5% NaCl was injected into the porous medium. In the case of run 11

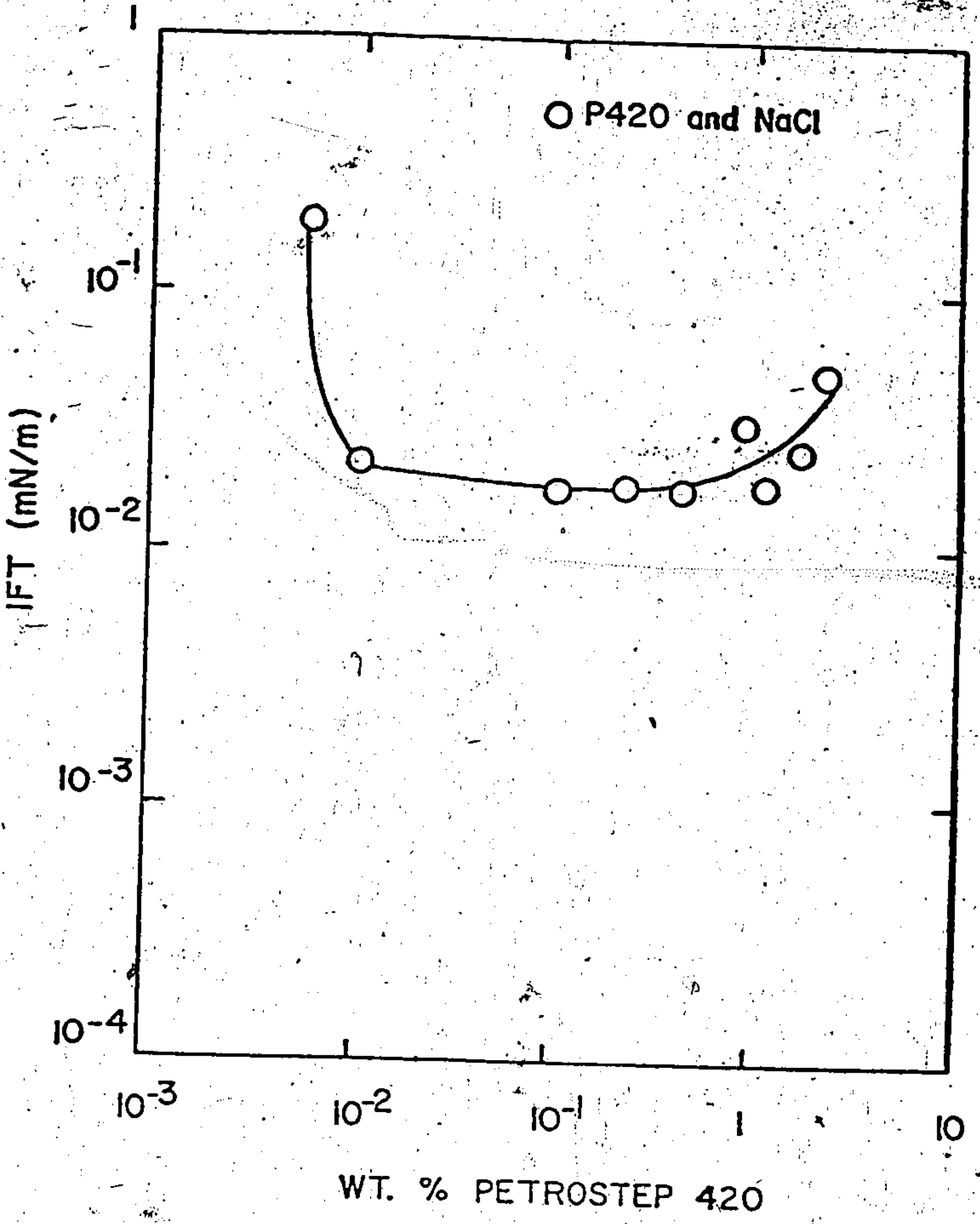


Figure 39- : Dependence of IFT on Total Surfactant Concentration of Fixed 1.5% NaCl Solutions (35)

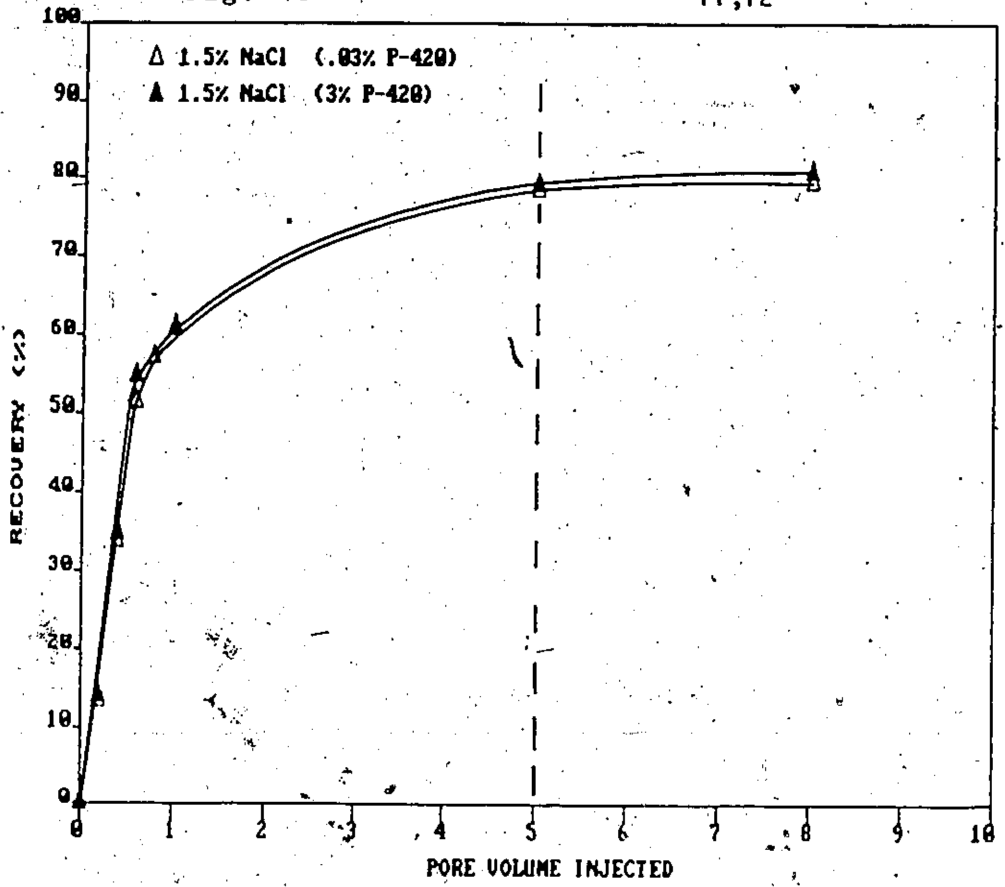
STRATEGY		
	SECONDARY	5 PV C.W.
	TERTIARY	3 PV SURFT.

H

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (5 P.V.)				TERTIARY REC. (8 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	5 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	8 PV (%)
11	1.5% NaCl .03% P-420	34.28	1.58	92.16	.256	5.13	.011	60.94	78.43	.086	.666	79.31
12	1.5% NaCl 3.0% P-420	34.28	1.64	90.43	.256	5.13	.011	60.45	78.98	.086	1.330	80.45

Fig. 40- PRODUCTION HISTORY RUN NO.: 11,12



this solution contained only 0.03% surfactant and in run 12 it contained 3% P-420. Since there were no divalent ions present, no precipitation or ganglia formation occurred. The 1% higher recovery with the more concentrated surfactant could be attributed to the greater viscosity of this displacing phase.

Experiments 7 and 8 were next performed (Fig. 41) with a surfactant solution containing 1% P-420 and as usual 1.5% NaCl. The connate waters were the ones used in most experiments, namely 1.5% NaCl on one hand, and 1.5% NaCl, 4.8% $CaCl_2$ and 1.6% $MgCl_2$ on the other hand. At the end of the secondary recovery almost 75% of the OOIP has been replaced by the corresponding connate waters. However, the production curve of experiment 8 (containing divalent ions) shows a sharp increase in recovery during tertiary surfactant flooding which could be attributed to precipitate formation and pore blockage effects as described in Section 7.2.

Experiments 8 and 10 (Fig. 42) involved similar connate waters containing equal amounts of divalent as well as monovalent ions. By the end of secondary waterflooding, in both cases about 75% of the OOIP had been produced. However at the end of tertiary recovery there was more oil recovered in the case where the less concentrated (1%) surfactant was used. Although this difference was only about 1% (relative tertiary recoveries are 18.6 and 15.7%, a difference of 3.2%), in

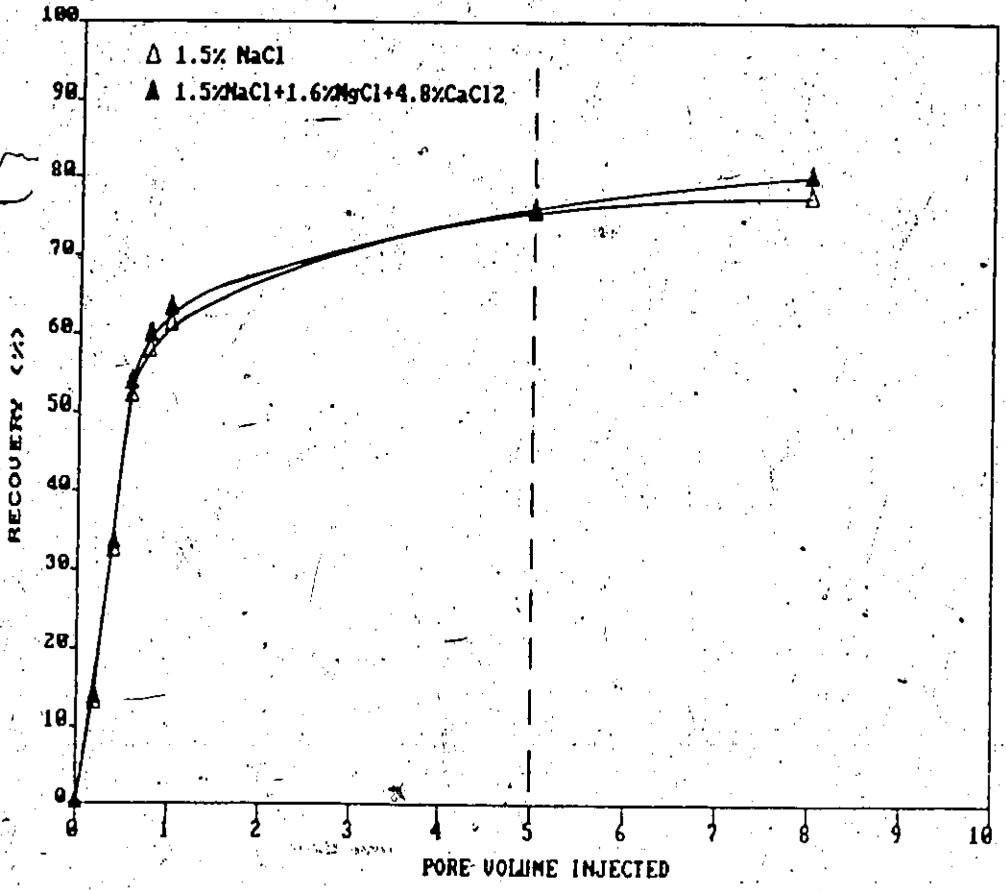
STRATEGY		
	SECONDARY	5 PV C.W.
	TERTIARY	3 PV SURFT. 1%

H

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (5 P.V.)				TERTIARY REC. (8 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	5 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	8 PV (%)
7	1.5% NaCl	34.28	1.75	92.05	.256	5.13	.011	61.01	75.41	.086 ?	.892 ?	77.46
8	1.5% NaCl 1.6% $MgCl_2$ 4.8% $CaCl_2$	34.20	1.74	91.16	2.058	4.22	.017	63.01	75.49	.355 ?	.216 ?	80.05

Fig. 41 - PRODUCTION HISTORY RUN NO.: 7,8

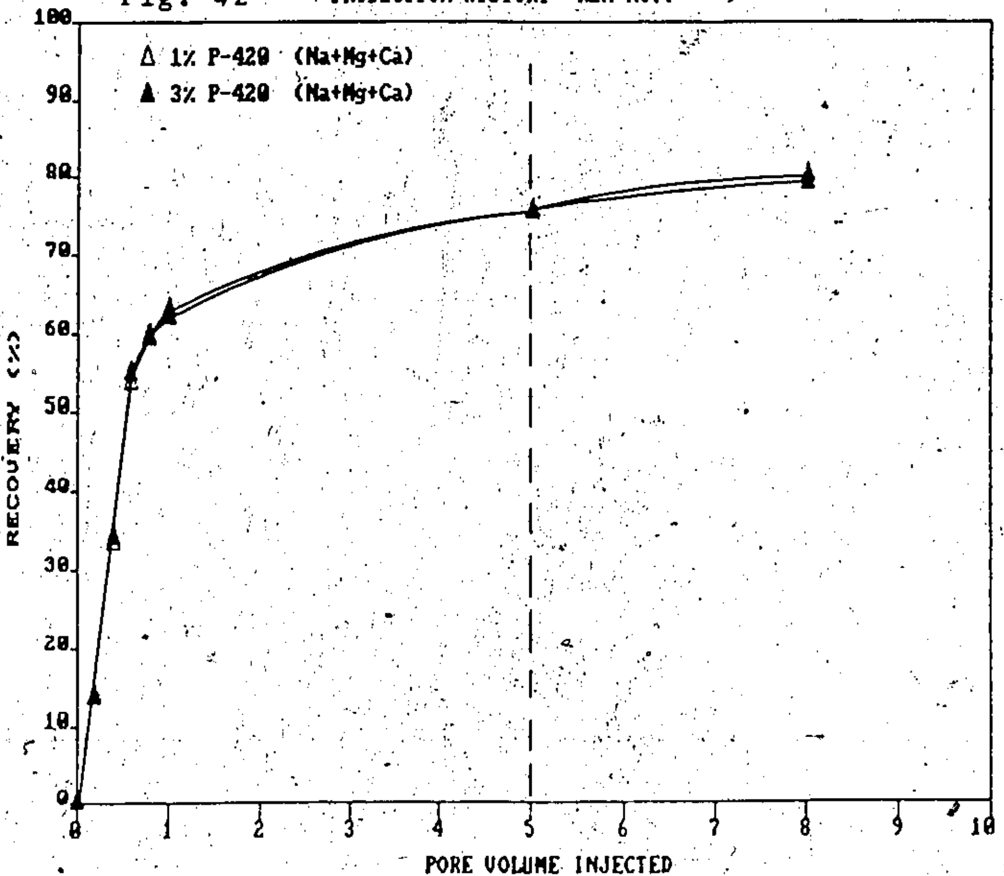


STRATEGY	SECONDARY	5 PV C.W.
	TERTIARY	8 PV SURFT.

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm²	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (5 P.V.)				TERTIARY REC. (8 P.V.)		
						I.F.T mN/m	N_{ca} ×10³	1 PV (%)	5 PV (%)	I.F.T mN/m	N_{ca} ×10³	8 PV (%)
8	Na,Mg,Ca SUR: 1%P-420	34.20	1.74	91.16	2.058	4.22	.017	63.01	75.49	.355	.216	80.05
10	Na,Mg,Ca SUR: 3%P-420	34.20	1.54	90.64	2.058	4.22	.017	62.10	75.16	.355	.322	78.98

Fig. 42 - PRODUCTION HISTORY RUN NO.: 8,10



large-scale recovery projects: this could translate into millions of dollars. At any rate, we believe the reason for lower recovery with more concentrated surfactant might be the redissolution mechanism proposed by Celik (40). To be more precise, at the end of tertiary recovery in experiment 10, the concentration of the surfactant has been constantly increasing (in the beginning of surfactant flooding due to dilution effects, the real concentration of surfactant is practically less than 3%) and this might redissolve some of the precipitates formed in earlier stages of tertiary recovery when the concentration of the surfactant was still less than 3%. Consequently, there would be fewer pores blocked with the precipitate, resulting in a lower recovery.

To further investigate the pore blockage phenomenon, we conducted experiments in which the so-called tertiary recovery involved displacement of oil by solutions of inorganic salts (instead of surfactants) known to form insoluble precipitates with divalent ions. These inorganic salts are not known to have any surface activity and therefore would not change the IFT between the oil and water phases. One of the more interesting salts was sodium carbonate which would react with calcium or magnesium chloride to form insoluble $CaCO_3$ and $MgCO_3$ precipitates according to the following reactions :

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3\downarrow + 2NaCl$$

$$Na_2CO_3 + MgCl_2 \longrightarrow MgCO_3\downarrow + 2NaCl$$

Experiments 13 and 14 (Fig. 43) were performed using our two typical systems (one containing NaCl and the other $CaCl_2$, $MgCl_2$ as well as NaCl). 5 PV of waterflooding resulted in a 3% higher recovery for the system lacking divalent ions. The so-called tertiary recovery was then started using a 5% (wt) solution of Na_2CO_3. As soon as the sodium carbonate solution came into contact with the porous medium containing divalent ions, a white precipitate was formed. The tertiary recovery of run 13 was higher than that of run 14 (relative recoveries of 13.68 compared to 5.59%). The formation of $CaCO_3$ and $MgCO_3$ precipitates and subsequent pore blockage effects in the case where divalent ions were present explains these results.

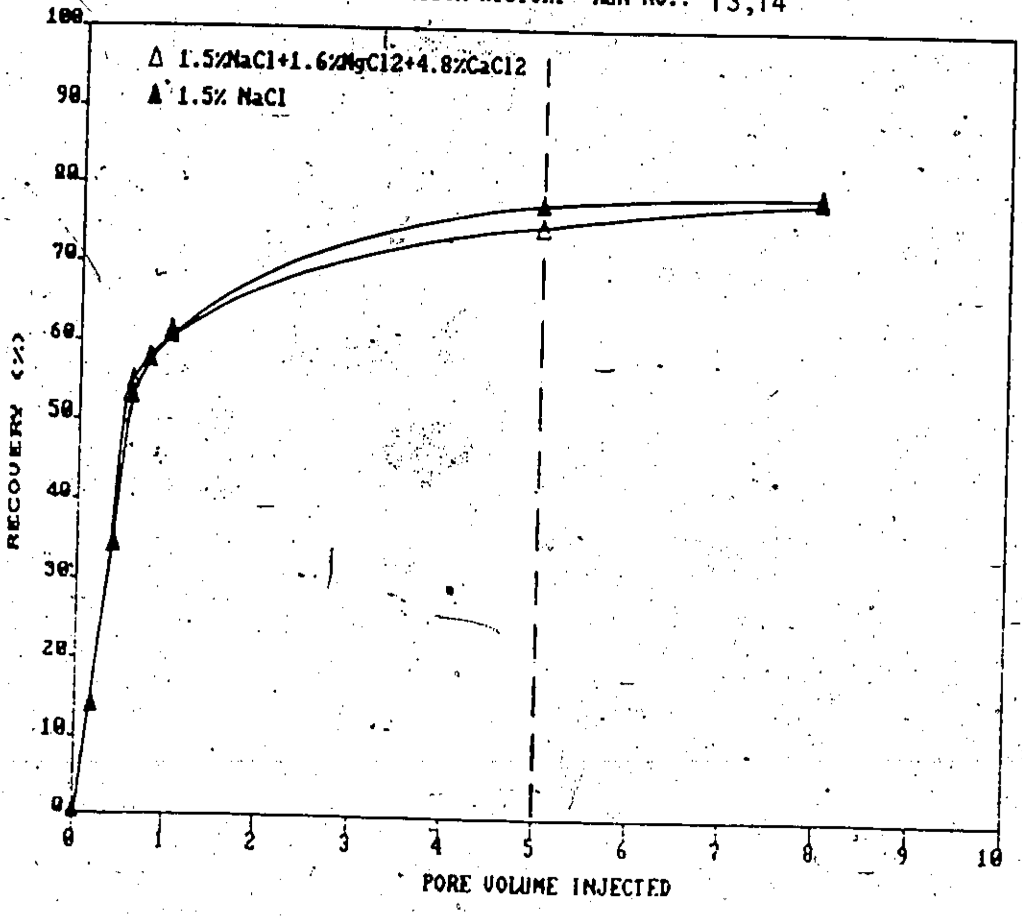
In another experiment (run 16 - Fig. 44) a connate water similar to that of run 13 (containing divalent ions) was used. However, in this experiment the tertiary flood contained only 1% Na_2CO_3. As we can see from the production curve of Figure (44), the amount of oil recovered during tertiary (sodium carbonate) flooding is greater in the case where a 5% solution of Na_2CO_3 was used (relative recoveries of 13.68

STRATEGY		
	SECONDARY	5 PV C.W.
	TERTIARY	3 PV Na_2CO_3 5%

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	φ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (5 P.V.)				TERTIARY REC. (8 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	5 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	8 PV (%)
13	1.5% NaCl 1.6% $MgCl_2$ 4.8% $CaCl_2$	34.44	1.70	90.25	2.058	4.22	.017	60.99	74.46	---	---	77.95
14	1.5% NaCl	34.12	1.36	91.31	.256	5.13	.011	60.20	77.31	---	---	78.58

Fig.43 - PRODUCTION HISTORY RUN NO.: 13,14

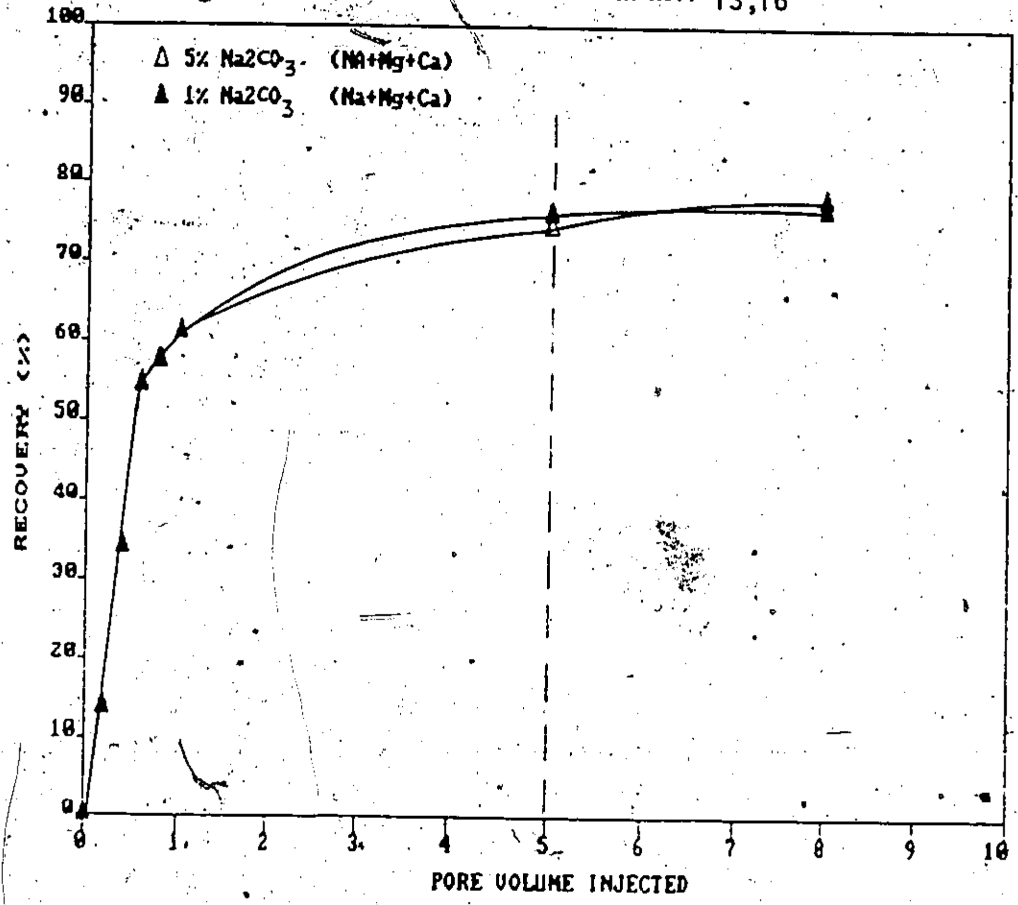


STRATEGY	SECONDARY	5 PV C.W.
	TERTIARY	3 PV Na_2CO_3

DISPLACEMENT TEST DATA

RUN NO.	SYSTEM CONNATE WATER	ϕ (%)	K μm^2	INIT. OIL SAT.	I.S. gMol/lit	SECONDARY REC. (5 P.V.)				TERTIARY REC. (8 P.V.)		
						I.F.T mN/m	N_{ca} $\times 10^3$	1 PV (%)	5 PV (%)	I.F.T mN/m	N_{ca} $\times 10^3$	8 PV (%)
13	Na,Mg,Ca Na_2CO_3 5%	34.44	1.70	90.25	2.058	4.22	.017	60.99	74.46	---	---	77.95
16	Na,Mg,Ca Na_2CO_3 1%	34.12	1.64	90.85	2.058	4.22	.017	60.82	76.17	---	---	76.88

Fig. 44 - PRODUCTION HISTORY RUN NO.: 13,16



compared to 3.20%). The reason is that the amount of precipitate formed in run 16 was less than that formed in run 13. Consequently, there is going to be less pore blockage when a 1% solution of Na_2CO_3 was used which in effect results in a lower oil recovery. We should not, however, ignore the fact that some of this higher recovery with 5% solution of Na_2CO_3 might be caused by greater viscosity of the latter solution as compared to that of the first one. this would result in a better sweep efficiency and a higher oil recovery.

CHAPTER X

CONCLUSIONS

1- In the absence of surfactants, the IFT between the oil and water containing NaCl had the highest values followed by that of the oil and connate waters containing $CaCl_2$ and $MgCl_2$.

2- In the presence of a 0.2% (wt) solution of P-420 surfactant, the IFT between the oil and connate water containing $CaCl_2$ was the highest. The connate water containing $MgCl_2$ produced the second highest IFTs and that with NaCl the lowest of all.

3- Divalent ions would make the porous medium more water-wet. Therefore, the oil would occupy the large pores in the form of blobs and ganglia relatively easy to recover. In the absence of divalent ions, the porous medium would be more oil-wet. The oil would primarily occupy small pores and would form a thin layer on the surface of the solid particles. This strong attachment onto the surface would make it difficult to recover oil from these oil-wet porous media.

4- In the absence of divalent ions, the penetration of the displacing fluid into the oil phase produced many small and thin fingers without any major ganglia. When divalent ions were present, the fingers were very large and irregular. Many oil ganglia and blobs were formed. These irregularities were more obvious in the case of $MgCl_2$.

5- Divalent ions would cause the precipitation of the petroleum sulfonate. An increase in the concentration of either the salt or the surfactant would increase the amount of these precipitates. This precipitate is a high viscosity sticky material quite capable of partially or completely blocking the pores, in which case flow through the other pores (containing oil) would be increased resulting in higher oil recovery. Monovalent cations (at least in the concentration range used in this project) did not form precipitates with the petroleum sulfonate.

6- The existence of divalent ions in the connate water would cause a higher oil recovery from such pores due to the pore blockage phenomenon. This mechanism has been further investigated and confirmed by injection of Na_2CO_3 (instead of surfactant) and subsequent formation of $CaCO_3$ precipitates.

7- The degree of precipitation and pore blockage would increase with the concentration of surfactant and so would the oil recovery. However, a point would be reached where the concentration of surfactant is high enough for redissolution processes to start, in which case the amount of precipitate and the level of pore blockage would both begin to decrease resulting in a reduction in oil recovery.

8- Oil recovery from a porous medium is a very complex process. Although one may investigate the individual contribution of such factors as IFT, N_{ca}, IS, contact angle, pore blockage effect, ganglia formation, etc., it is extremely difficult to express the size of each contribution with high degrees of certainty. In other words, the outcome of the displacement tests depends upon many factors and it is the ensemble of these factors that will determine the result of the oil displacement process.

CHAPTER XI

RECOMMENDATIONS

Based on the findings of this research project, the following recommendations are made :

A)-Further study could be conducted in these areas :

1- More detailed studies of wettability and contact angle behavior of such systems should be performed in close conjunction with displacement studies. This would reveal more information about the complex mechanisms involved in such displacement processes.

2- Complete and thorough studies of electrochemical properties of the various electrolyte systems used in our study should provide useful information about such things as zeta potential, attractive and repulsive forces, etc..., enabling future researchers to have a better understanding of oil recovery mechanisms from the electrochemical point of view.

3- Possibility of performing experiments under more realistic conditions such as at higher temperatures and pressures should be considered.

4- Possibility of conducting displacement experiments with heavier oils such as Lloydminster and Cold Lake oils should also be studied.

B)-Possible improvement of the displacement set up :

1- Since the group has just purchased a core flooding facility, I would strongly suggest that future displacement tests be conducted with this new equipment, in which case the porous medium does not have to be changed from experiment to experiment. In addition, the temperature-pressure conditions would also be easier to manipulate.

2- The pressure drop measurements should be performed using more accurate equipment such as differential pressure transducers.

3- The produced fluids should be analyzed with more reliable and precise instruments such as the spectrophotometer or the high pressure separator.

CHAPTER XII

NOMENCLATURE

A) Abbreviations :

EOR	Enhanced Oil Recovery
IFT	Interfacial Tension (mN/m)
IS	Ionic Strength
OOIP	Original Oil In Place
PV	Pore Volume
WOR	Water/Oil Ratio

B) Mathematical Expressions :

A	Core holder cross sectional area, Cm^2
C	Concentration, (wt%)
c	Molar concentration, mole/lit
d	Density, Diameter of the droplet
d_p	Volumetric diameter of the pore chamber
K	Permeability, m^2
L	Core holder length, Cm
M	Mobility ratio
N_{ca}	Capillary number

P_c	Capillary pressure, Atm
Q	Aqueous phase flow rate, Cm^3/Sec
r	Radius of the curvature, Cm
S_{ri}	Irreducible oil saturation, %
S_{wi}	Irreducible water saturation, %
S_{oi}	Initial oil saturation, %
S_{or}	Residual oil saturation, %
T	Reciprocal of angular velocity
u	Velocity, Cm/min
V	Velocity, Cm/min
x	Length of the porous medium
Z	Valency of ions

C) Greek Symbols :

λ	Mobility
Π	Spreading pressure, Atm
μ	Viscosity, cp
ΔP	Pressure drop across a certain length of the porous medium, Atm
ϕ	Porosity
ΔP_{neck}	Pressure drop across the neck of a finger, Atm
$\Delta\rho$	Density difference between the oil and water phases
γ	Interfacial tension, mN/m
θ	Contact angle, degrees

D) Subscripts :

a	Air
l	Liquid
o	Oil
s	Solid
w	Water

CHAPTER XIII

BIBLIOGRAPHY

1. "Basic Petroleum Data Book", American Petroleum Data Book (1984).
2. Jha, K.N., Chemistry in Canada, 34, 19, (1982).
3. Prince, J.P., Cnd Energy Research Institute, Calgary, Mar. 1980, 9 .
4. Neale, G., "Interfacial Phenomena in Engineering CHG 8196" Dept. of Chem. Eng. , U of Ottawa , (1985).
5. Bansal, B., M.A.Sc. Thesis, Dept. of Chem. Eng., , U of Ottawa, (1978).
6. Babu, D.R., Hornof, V. and Neale, G., Cnd. J. of Chem. Eng 62, 156, (1984) .
7. Mungan, N., Soc. of Pet. Eng. J., Feb. 1966, 247 .
8. Taber, J.J., Pure and Applied Chem. 52 , 1323 , (1980).
9. Shah, D.O., Third European Symp. on EOR , U.K. , Sept. 1981, Fayers, F. J., Ed., Elsevier Sci. Pub. Co., Chap. 1, (1981).
10. Reive, D.M., M.A.Sc. Thesis, Dept. of Chem. Eng., U. of Ottawa, (1985).
11. Melrose, J.C., and Brandner, C.F., J. Cnd. Pet. Tech., 14 , 56, (1974).
12. Foster, W.R., J. Pet. Tech. 25, 205, (1974).
13. Leonard, J., Ed., Oil and Gas J., Apr. 1984, 83 .

14. Forbes, R.J., "Studies in Early Petroleum History", Leiden, Netherlands, 52, (1958).
15. Squires, F., "Method of Recovery, Oil and Gas", U.S Patent No. 1,238,355.
16. Wyckoff, R.D. and Botset, G.H., Physics, 7, 325 (1936).
17. Uren, L.D., and Fahmy, E.H., Trans. AIME, 77, 318 (1927).
18. Benner, F.C., Riches, W.W., and Bartell, F.E.,"API Drilling and Production Practice" , (1938).
19. Jamin, J.M., Compt. Rend., 50,172 (1860).
20. Morrow, N.R., J. Cnd. Pet. Tech., 15, 49, (1976).
21. Moore, T.F. and Slobod, R.L., Prod. Monthly, 20, 20, (1956).
22. Reisberg, J. and Doscher, T.M., Prod. Monthly, 21, 43, (1956).
23. Wagner, O.R. and Leach, R.O., Trans. AIME, 216, 65 (1959)
24. Graue, D.J. and Johnson, C.E., J. Pet. Tech. 1365, (1974)
25. Taber, J.J., Trans. AIME, 213, 186, (1959).
26. Cayias, J.L.,J. Coll. and Int. Sci., 59, 39 (1977).
27. Cash, R.L., Cayias, J.L., Fournier, G., Jacobson, J.K., Schares, T., Schechter, R.S., and Wade, W.H., J. Coll. and Int. Sci., 59, 39 (1977).
28. Harkins, W.D., and Zollman, H., J. American Chem. Soc., 48, 69, (1926).
29. Hwan, R.N., Miller, C.A., and Fort, T., J. Coll. and Int. Sci., 68, 221, (1979).
30. Bansal, W.K., Shah, D.O., J. of Am. Oil Chem. Soc., 55,

No. 3, 367, (1978).

31. Jennings, H.T.Jr., Johnson, C.E., and McAuiliffe, C.D., J. Pet. Tech. , 26, 1344, (1974).

32. Cooke, C.E.Jr., Williams, R.E., and Kolodzie, P.A., J. Pet. Tech., 26, 1365, (1974).

33. Kumar,A., Neale, G. And Hornof, V., J. Cnd. Pet. Tech., Jan.-Feb. 1984, 37 .

34. Chiwetelu, C.I., M.A.Sc. Thesis, Dept. of Chem. Eng., U. of Ottawa, (1979).

35. Margeson, J., M.A.Sc. Thesis , Dept. of Chem. Eng., U. of Ottawa, (1982).

36. Dranchuk, P.M., Scott, J.D., and Flock, D.L., J. Cnd. Pet. Tech., 13, 1, (1974).

37. Hirasaki, G.J., and Lawson, J.B., SPE 10921, SPE-AIME 57th. Ann. Fall Conf., New Orleans L.A., (1982).

38. Trogus, F.G., Sophany, J., Schechter, R.S. and Wade, W.H. , Soc. of Pet. Eng. J., Oct. 1977, 337 .

39. Cayias, J.L., Schechter, R.S. and Wade, W.H., ACS Symp. Ser., No. 8, 234, (1975).

40. Celik, M.S., Manev, E.D. and Somasundaran, P., AIChE. Symp. Ser. 78, No. 212, 86, (1982).

41. Hirasaki, G.J., Soc. of Pet. Eng. J., Dec. 1982, 971 .

42. Glover, C.J. Puerto, M.C., Maerker, J.M. and Sandvik, E. L., Soc. of Pet. Eng. J., Jun. 1979, 183 .

43. Bansal, V.K., and Shah, D.O., J. Coll. and Int. Sci., 65 No. 3 , 451 (1978) .

44. Payatakes, A.C., Ann. Rev. Fluid Mech. 14, 365, (1982).

45. Mohanty, K., Davis, H.T., Scriven, L.E., SPE 9406, SPE-AIME Ann. Conf., Dallas, Texas, (1980).

46. Nutting, P.G., Oil and Gas J., 27, 22-146-238, (1928).

47. Reed, R.L., and Healy, R.N., "Improved Oil Recovery by Surfactant and Polymer Flooding" Shah, D.O., and Schechter, R.S., Eds. Academic Press, 383, N. Y. , (1977) .

48. Latil, M., "Enhanced Oil Recovery", Chap. 2, Paris, 1980.

49. Berger, B.D., Anderson, K.E., "Modern Petroleum", Pennwell Books, Oklahoma, (1981).